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#### AIR FORCE CAMBRIDGE RESEARCH LABORATORIES

L. G. HANSCOM FIELD, BEDFORD, MASSACHUSETTS

## AFCRL Atmospheric Absorption Line Parameters Compilation

R.A. McCLATCHEY W.S. BENEDICT S.A. CLOUGH D.E. BURCH R.F. CALFEE K. FOX L.S. ROTHMAN

J.S. GARING

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### OPTICAL PHYSICS LABORATORY PROJECT 7670 AIR FORCE CAMBRIDGE RESEARCH LABORATORIES

L. G. HANSCOM FIELD, BEDFORD, MASSACHUSETTS



## AFCRL Atmospheric Absorption Line Parameters Compilation

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R.A. McCLATCHEY W.S. BENEDICT\* S.A. CLOUGH D.E. BURCH † R.F. CALFEE K. FOX ‡ L.S. ROTHMAN J.S. GARING

- \* University of Maryland
- † Philco Ford Corporation
- # University of Tennessee

AIR FORCE SYSTEMS COMMAND
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#### **Abstract**

The report describes a compilation of the molecular spectroscopic parameters for a number of infrared-active molecules occurring naturally in the terrestrial atmosphere. The following molecules are included in this compilation: water vapor; carbon dioxide; ozone; nitrous oxide; carbon monoxide; methane; and oxygen. The spectral region covered extends from less than 1  $\mu$ m to the far infrared, and data are presented on more than 100,000 spectral lines. The parameters included in the compilation for each line are: frequency, intensity, half-width, energy of the lower state of the transition, vibrational and rotational identifications of the upper and lower energy states, an isotopic identification, and a molecular identification.

A discussion is provided separately for each molecular species, indicating the sources and accuracy of the data and a general discussion of how the data were obtained.

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## AFCRL Atmospheric Absorption Line Parameters Compilation

#### 1. INTRODUCTION

About 10 years ago a program was initiated to compile spectroscopic data on individual vibration-rotation lines of water vapor in the 2.7  $\mu$ m region (Gates, et al, 1964).

This work continued resulting in a publication on the 2.05 and 2.7  $\mu$ m bands of carbon dioxide (Calfee and Benedict, 1966) and a third publication on the 1.9 and 6.3  $\mu$ m bands of water vapor (Benedict and Calfee, 1967). Other workers have published similar results on the 15  $\mu$ m bands of CO<sub>2</sub> (Drayson and Young, 1967), the 9.6  $\mu$ m bands of O<sub>3</sub> (Clough and Kneizys, 1965), the CO bands whose fundamental is near 5  $\mu$ m (Kunde, 1967), the CH<sub>4</sub> bands near 3 and 7.5  $\mu$ m (Kyle, 1968) and the unpublished rotational water data calculated by Benedict and Kaplan in 1959 (see Goody, 1964, p. 184).

About 5 years ago an effort was initiated at AFCRL to continue this work with the aim of providing a complete set of data for all vibration-rotation lines of all naturally occurring molecules of significance in the terrestrial atmospheres. With such data at hand, it would be possible to compute the transmittance appropriate for atmospheric paths by first computing the monochromatic transmittance many times in a finely spaced frequency grid and then degrading the results to any appropriate spectral resolution. Up to now the following molecules have been included in this compilation: (1) water vapor; (2) carbon dioxide; (3) ozone; (4) nitrous oxide; (5) carbon monoxide; (6) methane; and (7) oxygen.

(Received for publication 26 January 1973)

All of these molecules except oxygen are minor constituents of the atmosphere, but nonetheless represent most of the absorption lines in the visible and infrared. Although there is some evidence for decreasing concentration with height of  $N_2O$ , CO, and  $CH_4$ , it is probably reasonable for most purposes to assume that all of these gases except  $H_2O$ , and  $O_3$  are uniformly mixed by volume in the atmosphere unless other specific information is available. Table 1 provides concentrations and references for these "uniformly mixed gases". Water vapor and ozone are, of course, not uniformly mixed and an appropriate set of models useful in considering the radiation effects of these gases is provided by McClatchey, et al, 1972.

Constituent	ppm by volume	Reference
CO <sub>2</sub>	330	Fink et al, 1964
N <sub>2</sub> O	0.28	Birkland and Shaw, 1959
co	0.075	Shaw, 1968
CH <sub>4</sub>	1,6	Goody, 1964
0,	$2.10 \times 10^{5}$	Valley, 1965

Table 1. Concentrations of Uniformly Mixed Gases in Dry Air

#### 2. DESCRIPTION OF COMPILATION

In order to compute the transmittance due to a given spectral line in the atmosphere it is necessary to describe the absorption coefficient as a function of frequency for each line. The four essential line parameters for each line are the resonant frequency,  $\nu_0$  (cm<sup>-1</sup>), the intensity per absorbing molecule, S(cm<sup>-1</sup>/molecule cm<sup>-2</sup>) the Lorentz line width parameter,  $\alpha_0$  (cm<sup>-1</sup>/atm), and the energy of the lower state, E''(cm<sup>-1</sup>). The frequency,  $\nu_0$ , is independent of both temperature and pressure (except for possibly very small pressure effects of less than 0.01 cm<sup>-1</sup>/atm, which have been ignored here). The intensity, S, is pressure-independent, and, as discussed below, its temperature dependence can be calculated from E'' and  $\nu$ 

The line half-width at half maximum,  $\alpha$ , is by definition proportional to the pressure, p, and its temperature dependence can be estimated as discussed below.

The precise line shape is a matter of some uncertainty, but in the derivation of line parameter's from laboratory measurements, it is customary to start from the Lorentz shape (see Goody, 1964) given in Eq. (1).

$$k(\nu) = \frac{S\alpha}{\pi(\nu - \nu_0)^2 + \alpha^2}$$

$$S = \int k(\nu) d\nu$$
(1)

The validity of Eq. (1) to describe the true line shape is subject to two limitations. The first, which can be precisely estimated and corrected for by the use of the Voigt shape, occurs when  $\alpha_0$  P/ $\alpha_D$  < 1.0 where  $\alpha_D$  is the doppler line width which varies with frequency, temperature and molecular mass as given in Eq. (2).

$$\alpha_{\rm D} = \frac{\nu}{c} \left( \frac{2kT \ln 2}{m} \right)^{1/2} = 4.298 \times 10^{-7} \nu (T/M)^{1/2}$$
 (2)

where M = molecular weight and here k = Boltzmann's constant and m = mass of a molecule.

For atmospheric molecules and infrared frequencies, modifications of the Lorentz shape begin to be required at pressures below 10 to 100 mb.

The second limitation concerns possible inadequacies of the Lorentz shape, especially in the distant wings of a line ( $|\nu - \nu_0| >> \alpha$ ) (see Winters et al. 1964, and Burch et al. 1969) or when the long-range intermolecular forces responsible for collision broadening are dipole-quadrupole, leading to an exponent 1.75 rather than 2.0 for ( $\nu - \nu_0$ ), (Varanasi, 1972). Throughout this compilation we assume the validity of the Lorentz exponent.

The line intensity is temperature dependent through the Boltzmann factor and the partition function as indicated in Eq. (3) (the induced emission term has intentionally been omitted here),

$$S(T) = \frac{S(T_s)Q_v(T_s)Q_r(T_s)}{Q_v(T)Q_r(T)} \exp + \left[\frac{1.439E''(T-T_s)}{TT_s}\right]$$
(3)

where E'' (in cm<sup>-1</sup>) is the energy of the lower state of the transition and where  $Q_v$  and  $Q_r$  are the vibrational and rotational partition functions. The vibrational partition functions for the most abundant isotopes are given in Table 2. Partition functions for the other isotopes are similar. The temperature dependence of the rotational partition function is given by  $(T/T_s)^j$  where j is also provided in Table 2  $(T_s)^j$  is taken to be 296°K).

It is also necessary to know the temperature variation of  $\alpha$ . In the absence of specific indications discussed under each molecule, the equation  $\alpha$  (T)/ $\alpha$ (T) =  $(T/T_s)^{-n}$ , with n=1/2, corresponding to the assumption of temperature-independent collision diameters, may be made. The validity of the assumption is more uncertain, the larger the dependence of the diameter on the particular rotation-vibration transition, (that is, it is most unrealistic for  $H_2O$  and the low-J transitions of the other molecules). The theory of Tsao and Curnutte (1954) when applied to the determination of line width for  $H_2O$  lines gives a wide variation of n about the mean value of 0.62 (Benedict and Kaplan, 1959). Measurements made with a  $CO_2$  laser (Ely and McCubbin, 1970) indicate a value of n=1.0 for the P20 line of the 10.4  $\mu$ m  $CO_2$  band.

Table 2. Vibrational Partition Functions

Molecule	j	Tempera- ture	175	200	225	250	275	296	325
H <sub>2</sub> O	1.5		1.000	1.000	1.000	1.000	1.000	1.000	1.001
co,	1.0		1.0095	1.0192	1.0327	1.0502	1.0719	1,6931	1.1269
$O_3$	1.5		1.004	1.007	1,013	1.022	1.033	1.046	1.066
N <sub>2</sub> O	1.0		1.017	1.030	1.048	1.072	1.100	1.127	1.170
co	1.0		1.000	1.000	1.000	1.000	1.000	1.000	1.000
CH <sub>4</sub>	1.5		1.000	1.000	1.001	1.002	1.004	1.007	1.011
$O_2$	1.0		1.000	1.000	1.000	1.000	1.000	1.000	1.001

An examination of Eqs. (1) and (3) indicates that it is necessary to know the  $\nu_{\rm O}$ , S(T<sub>S</sub>),  $\alpha$ (P<sub>O</sub>, T<sub>S</sub>) and E" value for each line in order to compute a spectrum. The data compilation described here contains these four quantities for each of the more than 100,000 lines between 1  $\mu$ m and the far infrared belonging to the seven molecular species listed in Table 3. Additional identifying information is also supplied for each line as indicated below.

Table 3. Intensity Criteria for Lines Included in Compilation

Molecule	Identification No.	Criterion Intensity* Minimum at T=296K	Existing Intensity Minimum at T=296K
н <sub>2</sub> О	1	3 × 10 <sup>-27</sup>	3 × 10 <sup>-27</sup>
co <sub>2</sub>	2	$2.2 \times 10^{-26}$	$3.7 \times 10^{-27}$
$o_3^2$	3	$3.5 \times 10^{-24}$	$3.5 \times 10^{-24}$
$N_2^{\circ}O$	4	$3.0 \times 10^{-23}$	$4.0 \times 10^{-23}$
co	5	$8.3 \times 10^{-23}$	$1.9 \times 10^{-23}$
СН <sub>4</sub>	6	$3.3 \times 10^{-24}$	$3.3 \times 10^{-24}$
$O_2$	7	$3.7 \times 10^{-30}$	$3.7 \times 10^{-30}$

<sup>\*</sup>Units are cm<sup>-1</sup>/(molecule-cm<sup>-2</sup>)

In order to establish the "Criterion Intensity Minimum" values given in Table 3, an extreme atmospheric path was considered, assuming the gas concentrations specified in Table 1 and maximum concentrations over the path of 3  $\times$  10<sup>24</sup> molecules/cm<sup>2</sup> for water vapor and 1  $\times$  10<sup>20</sup> molecules/cm<sup>2</sup> for ozone. This extreme radiation path was the atmospheric path tangent to the earth's surface, and extending from space to space. Using this criterion, lines yielding less than 10 percent absorption at the line center would normally be omitted.

Although this absolute line intensity cutoff was established, it has not always been possible to achieve. In some cases it would have been unrealistic to push calculations to this limit when experimental confirmation fell far short. There are two specific areas in which this absolute cutoff has been violated: (1) In regions of very strong absorption, very weak lines above this absolute limit have been neglected; (2) Q-branch lines below this limit have occasionally been included where it is felt that the accumulation of many weak, closely spaced lines would still produce an appreciable absorption under some atmospheric circumstances. In some cases, (for example, CO<sub>2</sub>), sufficient laboratory measurements and theoretical work were available so that this limit was exceeded throughout the infrared.

In the past, line intensities have been defined in various units, different for each molecular species. It was common to define water vapor concentration in precipitable cm, or  $g/cm^2$ , in the path in question. On the other hand, the amount of  $CO_2$  and the other uniformly mixed gases in a path were often given in cm-atm of gas at STP. In order to unify the units and ultimately to lead to less confusion, we decided to use the more fundamental quantity, molecules/cm<sup>2</sup> as a measure of absorbing gas abundance along the path. The appropriate conversion factors are:

$$1 \text{ (cm-atm)}_{STP} = 2.69 \times 10^{19} \text{ molecules/cm}^2$$

$$1 \text{ g/cm}^2 \text{ of H}_2\text{O} = 3.34 \times 10^{22} \text{ molecules/cm}^2$$
.

It was also decided, as indicated in Table 3, to define line (and band) intensities at  $296^{\circ}$ K, the normal room temperature at which most measurements are made. Intensities of all bands are based on the total number of molecules of a given species of all isotopes in their normal abundance, not on the number of the particular isotope responsible for a given band. Isotopic abundance values for all molecules for which data are provided in the compilation are given in Table 4.

Half-widths of lines have been added where available. Details are discussed in the separate sections on individual molecules. In some cases, it is felt that insufficient data exist to warrant the inclusion of a variable half-width. In these cases, a mean, constant value has been inserted for each molecular species and values are given in Table 5.

A shorthand notation was adopted to identify the various isotopic species. It is easy to understand by considering the following examples for  $CO_2$ :  $^{16}O^{12}C^{16}O \equiv 626$ ,  $^{16}O^{13}C^{16}O \equiv 636$ , and for  $N_2O$ ,  $^{14}N^{15}N^{16}O \equiv 456$ , etc. This same type of code is used for the other five molecules.

Table 4. Isotopic Abundances

H <sub>2</sub> O	161 162 181 171	0.99729 0.000300 0.00204 0.000370	CH <sub>4</sub>	211 311 212	0.98815 0.01110 0.00060
CO <sub>2</sub>	626 636 628 627 638 637 828	0.98414 0.01105 0.00402 0.000730 0.0000452 0.00000820 0.00000412	02	66 68 67	0.99519 0.00407 0.00074
03	666 668 686	0.99279 0.00406 0.00203			
'N <sub>2</sub> O	446 456 546 448 447	0,99022 0,00368 0,00368 0,00202 0,00037			
со	26 36 28 27	0.98652 0.01107 0.00202 0.000369			

Table 5. Mean Half-width Values

Molecule	Half-width (cm <sup>-1</sup> /atm)	References
$\begin{array}{c} {\rm CO_2} \\ {\rm O_3} \\ {\rm N_2O} \\ {\rm CO} \\ {\rm CH_4} \\ {\rm O_2} \end{array}$	0.07 0.11 0.08 0.06 0.055 0.060	Yamamoto et al (1969) Lichtenstein et al (1971) Toth (1971) Bouanich and Haeusler (1972) Varanasi (1971) (see Section 6.3) Burch and Gryvnak (1969)

A standard computer format was adopted for card or card-image input and is outlined below, the numbers between vertical lines representing the columns on an IBM card, and the letter-number combinations representing the computer format.\* The first four quantities are:  $\nu$  = frequency in

<u>v</u>		<u>α</u>	. —	Vibration ID	Date	Isotope	Molecule
	11-20 E10.3				71 -73 13	74-77 I4	78-80 I3

<sup>\*</sup>In the far infrared ( $\nu$  < 100 cm<sup>-1</sup>) a different format (F10.6) was occasionally chosen for the frequencies where high accuracy microwave measurements are available.

wavenumbers, S = line intensity in cm<sup>-1</sup>/molecule-cm<sup>-2</sup> at  $296^{\circ}$ K,  $\alpha = half$ -width in cm<sup>-1</sup> atm at  $296^{\circ}$ K, E'' = energy of the lower state expressed in wavenumbers. The rotation and vibration identification are the most difficult to unify due to the differences in the quantum numbers required to define the upper and lower states for different kinds of molecules. The columns 36 through 70 are indicated below for water and ozone, both triatomic asymmetric molecules, where (') indicates upper state and ('') indicates the lower state.

On the other hand, the quantum numbers specified for  $\mathrm{CO}_2$  and  $\mathrm{N}_2\mathrm{O}$  between columns 36 and 70 are given below, where again (') indicates upper state and ('') indicates lower state, and where r refers to Fermi resonance (see section on  $\mathrm{CO}_2$  for more details). The identification system for methane differs from those described here and is described in the section on methane.

$$v'_1v'_2 \ell'v'_3r'$$
  $v''_1v''_2 \ell''v''_3r''$   $P(J''+1)$   
2x 5x 5I2 A8

The remaining fields specified above include the entry date of the datum (important primarily for our purposes), the isotopic code as described above, and the molecular identification as given in Table 3.

This work has now proceeded to the point where most of the data consistent with the above-mentioned line intensity limitation are fairly complete in the 1  $\mu$ m to 100  $\mu$ m region. The nature of the remaining uncertainties and omissions is discussed in the sections to follow. The data are frequency ordered on magnetic tape and are contained in records of 321 ten-character words per record. An initial control word indicates the number of words to follow (320 for a full record). Each such record contains 40 card images in the format described above. Thus, it is necessary after reading a record from the tape to decode it according to the format I10, 40 (F10.3, E10.3, F5.3, F10.3, 5A6, A5, I3, I4, I3). In order to aid those using other than Control Data Corporation equipment, Table 6 is provided. The column headed "External BCD Code" indicates the character representation actually used on the tape. If a computer having a different character code is being used, a simple cross-referencing program must be constructed. End of file markers are placed on the tape at the following frequency points: 500, 1000, 2500, 5000, 10,000 cm with a double end of file appearing at the end of the tape.

In Appendix A we have included a listing of a computer program for directly reading the tape on a CDC 6600 computer. (No card decks are available.) For other computer systems the used is left to his own devices. Appendix B provides a computer program and output for generating a synthetic spectrum for a constant pressure path.

Table 6. CDC 6000 Series Fortran Character Codes\*

<u> </u>			
Source	Console	External	Punch Position
Language	Display	BCD	in a Hollerith
Character	Code	Code	Card Column
Character	Couc	Couc	0010 0010
A	01	61	12-1
В	02	62	12-2
C	03	63	12-3
D			12-4
	04	64	
E	05	65	12-5
F	06	66	12-6
G	07	67	12-7
H	10	70	12-8
I	11	71	12-9
J	12	41	11-1
K	13	42	11-2
L	14	43	11-3
	15	44	11-3
M			
N	16	45	11-5
0	17	46	11-6
P	20	47	11-7
Q	21	50	11-8
Ř	22	51	11-9
S	23	22	0-2
Ť	24	23	0-3
Ū	25	24	0-4
$\ddot{\mathbf{v}}$		25	0-5
	26		
W	27	26	0-6
X	30	27	0-7
Y	31	30	0-8
Z	32	31	0-9
0	33	12	0
1	34	01	1
2	35	02	2
3	36	03	3
4	37	04	4
5	40	05	5
6	41	06	6
7	42	07	7
8	43	10	8
9	44	11	9
+	45	60	12
<u> </u>	46	40	11
*	47	54	11-8-4
/	50	21	0-1
(	51	34	0-8-4
)	52	74	12-8-4
\$	53	53	11-8-3
<u> </u>	54	13	8-3
blank(space)	55	20	space
Dialik(Space)	56	33	space 0-8-3
, ,			
1	57	73	12-8-3

<sup>\*</sup>Taken from Control Data 6400/6500/6600 Fortran Reference Manual, Publication No. 60174900 Rev. C (1968) Control Data Corporation

Interested parties can obtain a copy of the data tape described here by mailing a new, 7-track, 800 BPI certified, 2400 ft long by 1/2 in. wide, magnetic tape to R. A. McClatchey, AFCRL (OPI), L. G. Hanscom Field, Bedford, Ma. 01730.

Due to the large amount of material included on this tape and the likelihood of errors, it is clear that the ultimate test of the accuracy and completeness of the data will be its use by many people in the scientific community. Therefore, we ask the cooperation of all who use these data to keep us informed of any apparent errors or omissions. We would appreciate the receipt of new laboratory data or theoretical work related to improving the data. We will then update this tape as sufficient new or revised data become available.

#### 3. GENERAL REMARKS ON THE DERIVATION OF PARAMETERS

The four tabulated parameters,  $\nu_{0}$ , E", S, and  $\alpha$  must of course be derived from experimental observations, subjected to data reduction in the framework of the general theories of molecular spectroscopy. For the basic theory we refer the reader to such textbooks as Herzberg (1950) and Goody (1964). The complexity needed to approach the problem depends both on the type of molecule and the accuracy of the observational data. We here outline the equations and methods used for the general types of molecules, linear triatomic (and diatomic)  $\mathrm{CO}_2$ ,  $\mathrm{N}_2\mathrm{O}$  and (CO); nonlinear triatomic,  $\mathrm{H}_2\mathrm{O}$  and  $\mathrm{O}_3$ . Methane,  $\mathrm{CH}_4$ , a spherical top, is a special case, as is the diatomic  $\mathrm{O}_2$ , where unpaired electrons complicate the rotational structure of the ground and excited electronic states.

The energy states and the transition probabilities between energy states of the molecules are defined primarily by their numerical values as established by experiments and by the indices (quantum numbers) which identify them. In nearly all the cases of interest, mathematical relations of greater or lesser complexity relate the numerical properties to the quantum numbers. We here present the general relations used to generate the tabulated data. The specific data and exceptional cases are discussed later for each molecule.

#### 3.1 Energy Levels and Line Positions

#### 3.1.1 LINEAR MOLECULES

For the triatomic linear molecules  $CO_2$  and  $N_2O$ , the vibrational states are characterized by three quantum numbers, which are zero or positive integers, of pure vibration,  $v_1$ ,  $v_2$ , and  $v_3$  and a fourth number  $\ell_2 = v_2$ ,  $v_2 - 2 \dots$  which represents the contribution of the bending mode to the angular rotation. In order to calculate the purely vibrational part of the energy ("the band origins"), it is necessary first to compute an unperturbed energy,

$$G_{v}^{unp}$$
, by:  $G_{v}^{unp} = \sum_{i} \omega_{i}^{vi} + \sum_{ij} X_{ij} v_{i} v_{j} + g_{22} \ell^{2} + \sum_{ijk} v_{i} v_{j} v_{k} + \sum_{ijk} v_{i} \ell^{2} + \dots$  (4)

and then to incorporate the effects of resonance perturbation by combining all close-lying levels with common  $\ell$  and common symmetry in matrices whose diagonal elements are  $G_V^{unp}$ , whose off-diagonal elements are functions of additional molecular constants and the four quantum numbers, and whose eigenvalues are the vibrational energy  $G_V^{unp}$ . For an excellent discussion and example, the reader is referred to the work on  $N_2O$  by Pliva (1968).

This perturbation calculation results in the "mixing" of states whose  $G_{V}^{unp}$  are particularly close, so that the final description of the level by the original four quantum numbers is a poor one. Accordingly, it is useful to add a fifth index, the rank symbol r to label in order of decreasing energy all such mixed states. We have adopted this procedure for  $CO_{2}$ , where the mixed states are  $(v_{1} \ v_{2} \ l_{2} \ v_{3})$ ,  $(v_{1} + 1, v_{2} - 2, l_{2}, v_{3})$ , . . . etc. The highest value of  $v_{1}$  and the lowest value of  $v_{2}$  in each set are retained in the vibrational indentification for all levels of the set.

In the present compilation, the above method was used to generate those energy levels which have not been observed; for all observed states the experimental value (averaged from various sources) was used.

The rotational energy of each vibrational state is given by:

$$E_{V,j} = G_V + B_V \left[ J(J+1) - \ell^2 \right] - D_V \left[ J(J+1) - \ell^2 \right]^2 + H_V \left[ J(J+1) - \ell^2 \right]^3 + \dots, (5)$$

where the constants  $B_v$ ,  $D_v$ ,  $H_v$  for each vibrational state are either determined by observation or calculated from a smaller number of rotational molecular constants. Whenever accurate constants have been observed, these are used; calculated values are reserved for the less important states. The equations for calculations of  $B_v$  and  $D_v$  are similar to those for  $G_v$ , and likewise require modification through the resonance perturbation. Evaluation from data of the small  $H_v$  constants requires highly accurate measurements extending to high  $J_v$ , so that in most cases these are fixed at zero; the non-zero values arise from resonances.

It will be noted in Eq. (4) that the vibrational energy depends on  $\ell^2$ . When  $\ell \neq 0$  there are two levels for each  $J \geq \ell$ , and this degeneracy is removed by rotation. The splitting (" $\ell$ -type doubling") results in two sets of levels, designated  $\underline{c}$  and  $\underline{d}$ , with different effective rotational constants. When  $\ell = 1$  the splitting is most important, and  $\underline{B}_c \neq \underline{B}_d$ ,  $\underline{D}_c \neq \underline{D}_d$ , etc.; when  $\ell = 2$ ,  $\underline{B}_c = \underline{B}_d$  but  $\underline{D}_c \neq \underline{D}_d$ , etc.; when  $\ell = 3$ , the constants other than H are the same. Resonances occasionally cause larger deviations.

When the linear molecule has a center of symmetry, as in  $CO_2$  with  $^{16}O$  at both ends (but not when one oxygen is isotopically different), the paired atoms with zero nuclear spin cause zero statistical weight for rotational levels of a given parity. Thus, only even-J levels exist for the ground vibrational level and for all other levels with  $\ell = 0$  and  $v_3$  even (" $r_g^+$  symmetry"); for levels with  $r_g^+$  o and  $r_g^+$  odd ( $r_g^-$ ), only J odd exists; when  $r_g^+$  odd levels are c and the J = even levels are d, etc. In the compilation symbols c or d are appended to the rotational quantum number of the lower state only when required, that is for  $r_g^+$  in the molecules without the center of symmetry. For example, R27C means  $r_g^+$  27c, Q27C means  $r_g^+$  27c.

The line frequencies are determined from the energy states by taking the differences corresponding to all allowed transitions. These depend on the familiar selection rules for the linear molecule:

When 
$$\Delta l = 0$$
,  $\Delta J = \pm 1$ ,  $c \rightarrow c$ ,  $d \rightarrow d$ .  
When  $\Delta l = 1$ ,  $\Delta J = \pm 1$ ,  $c \rightarrow c$ ,  $d \rightarrow d$ ,  
and  $\Delta J = 0$   $c \rightarrow d$ .

The line positions may thus be conveniently represented for computational purposes as given series in  $\underline{m}$ , where m = J'' + 1 for the R-branch ( $J'' \to J'' + 1$ ), m = -J'' for the P-branch ( $J'' \to J'' - 1$ ), and m = J'' for the Q-branch ( $J'' \to J'' - 1$ ). A different equation is needed for Q-branch of a given transition than for the P and R branches, because of the differences in the  $\underline{c}$  and  $\underline{d}$  constants. The general equation is

$$\nu (m) = G_{v} + am + bm^{2} + cm^{3} + dm^{4} + em^{5} + fm^{6}, \text{ with } a = (B'_{v} + B''_{v});$$

$$b = (B'_{v} - B''_{v} - D' + D''); c = -2 (D'_{v} + D''_{v}); d = -(D'_{v} - D''_{v});$$

$$e = 3(H'_{v} + H''_{v}); f = (H'_{v} - H''_{v}).$$
(6)

#### 3.1.2 NONLINEAR MOLECULES

The nonlinear triatomic molecules  $H_2O$  and  $O_3$  have similar basic structures. The formula for the vibrational energy is identical with Eq. (4), except that the quantum number  $\ell$  and its associated constants do not exist. Vibrational resonances exist; in both  $H_2O$  and  $O_3$ ,  $\omega_1 \sim \omega_3$ , but these are of different symmetry, so that interaction between the band origins and identical rotational states occurs only in (200,002), etc. In addition for  $H_2O$ , and much more closely for the 162 isotope,  $2\omega_2 \approx \omega_1$ , so that the properties of the higher vibrational levels must be computed by taking their resonances into account.

The rotational levels of these three-dimensional rotators, with three different reciprocal moments of inertia  $A_v > B_v > C_v$  are labelled by three quantum numbers, J,  $K_a$ ,  $K_c$ , with  $K_a$  and  $K_c$  assuming all values 0, 1, . . . J, subject to  $K_a + K_c = J$  or J + 1. There are thus 2J + 1 levels of a given J (each again with a rotational statistical weight of 2J + 1); in addition there is a nuclear-spin statistical weight which gives alternate levels, depending on the odd or even parity of  $J+K_a+K_c+v_3$ , weights of 3 or 1 for  $\mathrm{H}_2\mathrm{O}$ , 0 or 1 for isotopically symmetrical  $\mathrm{O}_3$ . The normal progressions of energy within each J is increasing with increasing  $K_a - K_c$ ; occasionally inversions of a few paired levels may occur in excited vibrational states as a result of rotation-vibration interactions between close-lying states of like over-all symmetry in different vibrational levels. As J increases, there is a tendency for the odd and even levels with K or K close in value to J to approach very closely in energy, so that many apparently single lines are in reality degenerate pairs with unresolvable spacings. The range of Ka, Kc in which these pairings occur, and the general spacing of the rotational levels is governed by the asymmetry parameter,  $\kappa =$ (2B-A-C)/(A-C), which for the ground vibrational states of  $\rm H_2O$ ,  $\rm HDO$ ,  $\rm O_3$  is respectively -0.437, -0.689, and -0.984. As the parameter approaches -1, the energy level formula approaches that of the symmetric top with A > B = C namely,

$$E_{r} = \frac{B+C}{2}J(J+1) + \left(A - \frac{B+C}{2}\right)K_{a}^{2} - D_{J}J^{2}(J+1)^{2} - D_{JK}J(J+1)K^{2} - D_{K}K^{4}$$
(7)

where the D's are centrifugal stretching constants, and where additional terms of powers higher in  $J^2$ ,  $K^2$  are often required. For the asymmetric top molecules with  $K \neq -1$ , the rotational energy cannot be given by a closed formula, but requires the construction and diagonalization of matrices whose diagonal elements are given by Eq. (7) whose off-diagonal elements involve B-C and two additional centrifugal stretching constants of power 4, etc., and whose eigenvalues are the rotational energy. From the eigenvectors of the diagonalization, one obtains effective angular moments about each axis,  $\langle P_a^2 \rangle$ ,  $\langle P_b^2 \rangle$ ,  $\langle P_c^2 \rangle$ , whose sum,  $P^2 = J(J+1)$  and one also obtains other coefficients necessary for the calculation of transition probabilities and other properties of each eigenstate.

The excited vibrational levels of water vapor may differ considerably from the ground state in their values of A, B, and C, and with a relatively high ratio of  $A/\omega_2$  (  $\simeq 0.018$ , as contrasted to 0.00059 for  $B/\omega_2$  in  $CO_2$ ), extensive overlapping occurs between rotational levels in nearby vibrational states, making the computation of the higher levels highly uncertain much beyond the limits of observation. Accordingly, for all except the lowest energy levels of the ground state it is preferable to use experimental rather than calculated values when available.

(11)

#### 3.2 Line Intensities

The intensity of any line at frequency  $\nu$  may be expressed in a purely formal way as:

$$S_{m} = \frac{\nu}{\nu_{0}} \cdot S_{v}^{o} \cdot S_{Rot} \cdot F \tag{8}$$

where So, is the vibrational intensity of a nonrotating molecule at the vibrational origin,  $\nu_{o}$  ;  $S_{Rot}$  is the rotational intensity for a rigid nonvibrating molecule and Fis a factor that takes into account the fact that both forms of motion are occurring simultaneously. In the rigid case, F = 1, and if  $S_{Rot}$  is normalized so that  $\Sigma_{\rm Rot}$  S<sub>Rot</sub> = 1 and if the band extends over a limited frequency range so that  $\nu/\nu_0$ ~1, then  $S_v^0$  as defined by Eq. (8) is identical with the quantity usually denoted by  $S_v$ . the total band intensity,  $\Sigma_{m}S_{m}$ .

 $\mathbf{S}_{Rot}$  consists of a temperature-independent factor, the rotational line strength,  $\mathbf{L}_{\mathbf{R}}$ , common to all linear molecules, and a temperature-dependent Boltzmann factor [Eq. (13)]. If the sum of all transitions from J" is normalized to the statistical weight g = 2J''+1, and if one recalls the definition of the rotational partition function  $Q_r(T) = \Sigma g \exp(-1.439E_R/T)$  (the summation is over all rotational levels of a given v), the normalization condition for all transitions ( $\Sigma S_{Rot} = 1$ ) is fulfilled.

The equations for  $L_{\mbox{\scriptsize R}}$  are as follows:

$$\Delta \ell$$
  $\Delta J$   $L_{R}$ 

0 0  $\ell^{2}(2m+1)/m(m+1)$  (9)

0  $\pm 1$  ( $|m| - \ell^{2}$ )/ $|m|$  (10)

+1 0 ( $|m| + 1 + \ell$ ) ( $m \mp \ell$ ) ( $2m + 1$ )/ $m(m + 1$ ) (11)

$$+1 +1 (|m| + 1 + \ell) (|m| + \ell)/|m| (12)$$

Equation (8) is exact with F = 1 only for a rigid molecule. In the actual molecule, a number of factors may cause deviations, which however will vary regularly along the band. (A very few exceptional situations, "crossing perturbations", may also be recognized.) Depending on the precision of the measurements, the nonrigidity corrections ("F-factors") for the linear molecule, may be expressed as regular functions of the running index, m, as indicated in Eq. (13).

$$F = S_{\text{nonrigid}}/S_{\text{rigid}} = (1 + am + bm^2 ...).$$
 (13)

The first order theoretical correction is  $F = (1 + \zeta m)^2$  or  $a = 2\zeta$ ,  $b = \zeta$ . For nearly all the intensities in the present compilation, a single  $\zeta$  was used for each vibrational band; this is included in the tabulations of band parameters. More

refined measurements and theoretical calculations should, in future revisions of this compilation, permit the use of additional terms in Eq. (13).

For asymmetric top molecules, many more transitions are possible from each rotational level J K  $_{\rm a}$ K  $_{\rm c}$ , but the same general definitions hold. The values of L  $_{\rm Rot}$  depend on the degree of asymmetry. Tabulations exist (Wacker, 1964) which are useful for orientation purposes. In the present work we either derive L  $_{\rm R}$  from the rotational constants, for pure-rotation bands and some fundamental bands, or make use of the tables.

The F-factor corrections to the intensities become of considerable significance for most of the vibration-rotation transitions in H<sub>2</sub>O. Various methods are used, based in part on theoretical considerations described later on, and in part on an arbitrary empirical adjustment of calculated values to the best observations.

A few general remarks should be made regarding the temperature dependence of S<sub>1</sub>°. S<sub>2</sub>° is proportional to the product of the relative population of the lower state, given by the vibrational Boltzmann terms exp (-1.439  $G_v$ )/ $Q_v$ , (with  $Q_v$  $\frac{\Sigma}{V}$  g<sub>V</sub> exp (-1.439G<sub>V</sub>) where g<sub>V</sub> is the degeneracy of the level, 1 when  $\ell$  = 0, 2 otherwise), and a temperature independent transition probability,  $u_{vv} = |\int \widetilde{\psi}_{vv} u \psi_{v}|^2 d\tau|^2$ ,  $\psi_{vv} = |\int \widetilde{\psi}_{vv} u \psi_{v}|^2 d\tau|^2$ being the dipole moment function, usually expressed as a Taylor's series expansion in the dimensionless normal coordinates. We rely on measurement to give the total absorption strength in a given spectral region. When the spectral resolution is sufficiently high to distinguish lines of the strongest band in the region, usually the one with the lower level v = 0, from lines of all of the weaker "hot" or isotopic bands which accompany it, no problems arise: The S. of each band, and accordingly the relative  $\mu_{vv}$  is empirically established (along with favorable cases a determination of coefficients of the F-factor, leading to  $\Sigma S_{\nu}$ for the region). However, most of the studies of quantitative band intensities have been made under conditions where only the total intensity is observed and the strengths of the weaker lines, which contribute only a few percent of the total, estimated from theoretical relations.

When all the transitions in the region are of the same type (that is, have identical  $\Delta v_1$ ,  $\Delta v_2$ ,  $\Delta v_3$ ,  $\Delta \ell$ ), a good approximation to the relative transition probability is to use harmonic oscillator wave functions and to assume that the leading term in the expansion of  $\mu$  is formed by the  $\Delta v$ 's: for example if  $\Delta v_1 = 2$ ,  $\Delta v_3 = 1$ , we require that this term be  $\mu_{113}$  q $_1^2$  q $_3$  with  $\mu_{113} = \frac{3}{9} \mu / \frac{3}{9} q_3$ . Evaluation of the integral for arbitrary values of  $v_1$ ,  $v_2$ ,  $v_3 \rightarrow v_1 + 2$ ,  $v_2$ ,  $v_3 + 1$  then gives the ratio  $\mu_{vv'}^2/\mu_{0.201}^2 = (v_1 + 2)!$  ( $v_3 + 1$ )!/ $v_1!v_3!$ . The general formula (for  $\Delta \ell = 0$ ) is  $(v_1 + \Delta v)!$  ( $v_2 + \Delta v$ )! ( $v_3 + \Delta v$ )!/ $v_1!v_2!v_3!$ . When  $\Delta \ell = \pm 1$  similar relations involving integers hold. Use of more realistic wave functions corrected for an

harmonicity with lower terms in the dipole expansion lead to very nearly the same ratios. Accordingly, for many transition regions this type of calculation is simple and acceptable.

When, however, as in the case of both CO, and N,O, the resonance perturbations mix the vibrational wavefunctions, a region includes several bands with different basic transitions. For example, the 1.6 µ region of CO2 contains four strong  $\Delta l = 0$  bands, composing the resonance quartet 3001r-0, with r=1, 2, 3, 4. If we assume that only the  $\Delta v_1 = 3$ ,  $\Delta v_3 = 1$  transition is involved, the relative transition probability of the four transitions should be given by the squared eigenvectors of the {301, 221, 141, 061} matrix, and the relative transition probability of the four hot transitions from 010 would be the same value (since  $\Delta v_2$  = 0) multiplied by the squared eigenvectors of the {311, 231, 151, 071} matrix. These are not identical with the other eigenvectors, and all four hot bands have different transition probabilities. Moreover, the observed ground-state intensities are not proportional to the first set of eigenvectors. Inclusion of a second basic transition integral for  $\Delta v_1 = 2$ ,  $\Delta v_2 = 2$ ,  $\Delta v_3 = 1$ , together with the appropriate eigenvectors can, however, bring the observations in accord with calculation, if the ratio  $\mu_{221}/$  $\mu_{301}$  is of the order of 0.1. The ratio 231-0/221-010 is 3, and accordingly its inclusion increases the over-all -010/0 strength ratio and further shifts the relative probabilities. As one extends the calculations to lower states involving resonating groups with  $v_2 = 2$ , 3, and higher, required in the stronger bands of  $CO_2$  and  $N_2O_3$ , the situation cannot be predicted in advance. However, calculations similar to those sketched above have been performed; then reliability depends on the accuracy of the input constants, but it is believed that such a computation is useful.

One must also note that in the isotopically modified molecules, the eigenvectors of resonating groups vary widely. Thus, the simple assumption of a constant isotopic abundance ratio for the intensities is very far from correct. It should be adequate however to assume that the relative intensities of the underlying transitions (301-0 and 221-0, in the example cited above) remain isotopically invarient.

It should also be remarked that the eigenvectors are rotationally dependent; the result would be a contribution to the m<sup>2</sup> term in Eq. (9).

#### 4. MOLECULAR SPECIES

#### 4.1 Water Vapor

#### 4.1.1 LINE POSITIONS

The frequencies of the lines of the principal isotope ( ${}^{1}H^{16}O^{1}H$  = Code 161) are calculated from a set of energy levels. These were obtained from the best available

data in all spectral regions by a smoothing process which is partly theoretical, partly empirical. The principal sources of data are identified and summarized in Table 7. The energy levels of the ground state,  $v_1 v_2 v_3 = 000$ , are by far the most extensive and accurate. They are based on a relatively small number (15, at the present writing) of microwave lines whose frequencies are precise to < 0.00001 cm<sup>-1</sup> (0.3 MHz), and several much larger groups of pure rotational lines, whose frequency accuracy may range from 0.001 to 0.002 cm<sup>-1</sup> for isolated lines measured with Michelson-type interferometers to 0.02 to 0.03 cm<sup>-1</sup> for weaker or partially blended lines measured with conventional spectrometers. With the long absorption paths available through the atmosphere, the observed lines extend to quite high energy levels, and by somewhat less accurate measurements with flame sources, to still higher levels, so that pure rotation transitions connect all levels from 0 to more than 4000 cm<sup>-1</sup>. The 000 level is the lower state of the more than 50 vibration-rotation bands observed between 900 and 20,000 cm<sup>-1</sup>, so that these measurements provide combination differences (common upper level in two or more transitions) for the 000 state that confirm, and for some states greatly improve those of the pure-rotation lines. In particular, the recent laboratory measurements of the 1.9  $\mu m$  region give low-J energy differences that are selfconsistent to better than 0.001 cm<sup>-1</sup>. A theoretical smoothing of the totality of the observed microwave, pure-rotation, and combination-difference data, by leastsquares fitting to a 29-constant Hamiltonian of the type described for D2O (Benedict et al, 1970) then yields the ground state energy levels used in the compilation. Inasmuch as none of the theoretical calculations have been successful in reproducing all of the available data to their apparent accuracy, the levels adopted for the current compilation are a calculated set for E < 2500 cm<sup>-1</sup>, and for higher energies are determined from observations. It is believed that the accuracy of lines involving these levels is  $\pm 0.005$  cm<sup>-1</sup> for E'' < 1500 cm<sup>-1</sup>;  $\pm 0.02$  cm<sup>-1</sup> for  $1500 < E'' < 3000 \text{ cm}^{-1}$ , and  $\pm 0.05 \text{ cm}^{-1}$  up to the tabulated limit. The levels of the other vibration-rotation states are then obtained by averaging the sums of the observed lines and the lower-state levels. When upper-state levels have not been observed, although transitions to them have expected intensities above the lower limit, estimated values are chosen, either by direct calculations using an appropriate approximate Hamiltonian, or by extrapolation of the observed series of upper-lower rotational energy differences.

For the isotopic forms 181 and 171, the ground-state energies were obtained in the same way, except with much less extensive data (respectively 12 and 9 microwave lines). The dependence on theoretical calculations for the smoothing is more extreme, and the data for levels higher than 1500 cm<sup>-1</sup>, the limit of observation, is quite uncertain. However, since the higher-order constants in the

Table 7. Summary of Principal Data Sources for Water-Vapor Energy Levels

		Range of	Leve	ls	Intensity	Precision	
Region	Type of			tional	•	of V	
cm <sup>-1</sup>	Measurement	Vibrational	J	Ка	(29€ K )	cm <sup>-1</sup>	Pef.
0-25	L,181,171	0,010	10	G	<-27	.00001	a,b
0-25	$L, \overline{162, 182}$	0,010	13	7	<-27	.00001	c,d
30-250	L	0	13	7	-23	.005	e
250-550	L	lo	15	11	-24	.03	f
480-690	LH	0	15	12	-25	.02	à
430-650	F	0,010 etc.	30	15	<-27	.05	h
700-1100	Lii	0,010	19	12	-26	.1	i
750-1400	A	0,010	18	12	-25	.05	j
860-1100	Α	0,010	18	12	-25	.02	k
1270-1450	LH	010,020	16	9	-27	.05	1
1200-1700	L,162	010	14	7	-27	.02	m
1330-1970	L, 181, 171	010	13	6	-26	.01	n
1840-2500	LH	010,020,001+	18	. 10	-26	.03	0,₹
1925-2182	A,U	010,020,001+	28	10	<-27	.01	p
2390-2970	A,U	100,001, etc.	32	19	<-27	.01	p
2480-3030	L,162	100,020	13	10	<-27	.005	q
2900-3500	Α	020,100,001	16	11	-26	.02	r
2800-3500	F	001,011, etc.	33	13	<-27	.02	s
2900-4330	L,162	001,100, etc.	14	9	-25	.005	t *
3340-4030	L,181,171	001,100, etc.	13	7	-26	.01	u
3940-4300	F	001,011, etc.	33	19	<-27	.02	s
4032-5090	A,U	001,011,020 +	33	17	<-27	.01	v
3950-5200	A	001,030,011,etd	18	13	-26	.01	w
4500-5915	L,162	011,030,110,etd		8	-25	.005	t *
5090-5575	L	011,110	12	7	-24	.005	x
5540-7000	A	011,021,120 +	16	9	-26	.01	w
5550-6720	A,U	011,021,120 +	24	11	<-27	.01	v
7000-7500	L	101,200	13	8	-24	.05	У
7400-9000	A	101,002,111 +	16	9	-26	.01	w
7390-8800	A,U	101,001,111 +	16	9	-25	.01	v
8300-10000	A	111,012,041	16	. 8	-25	.03	z
9150-9350	A	012,111	10	7	-27	.005	aa

#### References:

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- b. Steenbeckeliers et al, 1971
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- q. Benedict et al, 1973
- r. Beer, 1970
- s. Benedict and Sams, 1971;
- t. Pugh, 1972
- u. Fraley et al, 1969
- v. Hall, 1970
- w. Connes et al, 1969
- x. Flaud et al, 1972
- y. Nelson, 1951
- z. Swensson et al, 1970
- aa. Breckenridge and Hall, 1973

Table 7. References for Water Vapor Energy Level Data (Contd)

The data sources are of five types. L, laboratory absorption measurements on water vapor or moist air at room temperature; LH, similar measurements in cells heated to 75-540°C; F, laboratory measurements of emission from oxy-hydrogen or oxy-acetylene flames, yielding ~ $10^{19}$  molecules/cm²  $\rm H_20$  at +2500-3500K; A, measurements of solar radiation through the atmosphere, containing  $10^{22}$ - $10^{25}$  molecules/cm²; U, observations of the ratioed spectrum of sunspot/photosphere, also containing about  $10^{19}$  mol/cm² at ~3600K. Isotopic symbols are appended when enriched samples were studied, underlined when a major component, dashed when moderately increased above natural abundance. The range of vibrational and rotational levels is a rough indication of the extent of levels observable down to the intensity limit of S° (cm²/mol cm²), corrected to 296K, with the resolving power used. The ground state, (v=0) is implied in all regions.

\* In reference t, the observed contamination of the sample by deuterium to give the HDO abundances varying from 10-200 times normal was not reported.

theoretical fit were constrained near their values in  $\rm H_2O\text{-}161$ , the tabulated line positions for all pure-rotation lines should be accurate to  $\pm$  0.5 cm<sup>-1</sup>. Upper-state levels for these molecules are likewise available only for the strongest lines, so that the uncertainties of weak lines here might approach  $\pm$  1 cm<sup>-1</sup>.

The asymmetrically substituted HOD (162) molecule has been studied, both in the microwave and infrared regions with thoroughness comparable to 161, so that the frequency data, for the 000,010, 100, 020, 110, and 030 bands should be of the same accuracy as for 161. The 001 and 011 levels may have errors larger by a factor of five.

Quite reliable data can be calculated for the pure-rotation spectra of isotopic forms 182, 172, and 282, which are only of very minimal importance in the atmosphere. Weak lines in vibration-rotation bands of 182 (as yet unobserved, except for a few lines in 100-000) also have been included by estimating constant vibrational shifts from 162.

#### 4.1.2 LINE INTENSITIES

The intensities of pure rotation lines were calculated by a program in which the effects of vibration-rotation interaction on both the rotational eigenfunctions and on the dipole moment were included. The eigenfunctions were obtained from a Hamiltonian with 25 independent constants which gave an excellent fit to the energy levels, and the dipole moment was expressed as a linear expansion in the dimensionless normal coordinates:

$$\mu = \mu_e + (\partial \mu / \partial q_1)q_1 + (\partial u / \partial q_2)q_2 + (\partial \mu / \partial q_3)q_3 + \dots$$
 (14)

The  $\partial\mu/\partial q_i$  coefficients in this expression were obtained from the  $S_v^o$  values of the three fundamental bands by the equation  $S_{vi}^o$  = 4.  $16 \times 10^{-19} \, \nu (\partial \mu/\partial q_i)^2$ . The algebraic signs of  $\partial\mu/\partial q_i$  were chosen so that the observed vibration-rotation effects on intensities were reproduced in the fundamental bands of  $H_2O$  and verified by noting that these and only these choices also gave a reasonable fit to the band intensities and interaction effects in the isotopic molecules. The value of the permanent moment in the equilibrium configuration,  $\mu_e$  = 1.847D (Clough and Beers, 1973), was derived from Stark Effect measurements on 8 microwave lines in three isotopic water molecules (161, 162, 262), and is in excellent agreement with recent molecular-beam measurements (Dyke and Muenter, 1972). The uncertainty in the calculated intensities should result from inaccuracy of the  $\partial\mu/\partial q_i$  coefficients and neglect of higher terms in the expansion; accordingly, it should be of minor importance for low J lines, and is estimated to be less than 1 percent for E'' < 1000 cm<sup>-1</sup> and less than 10 percent for all lines in the tabulation, with the possible exception of the very low probability lines in such branches as  $R_{53}$ ,  $Q_{55}$ , etc. (Benedict, Classen and Shaw, 1952).

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The intensities of vibration-rotation lines are more difficult to calculate, because they differ from those of the rigid asymmetric rotor by three interrelated effects: (1) the centrifugal effects, as used above for pure rotation; (2) the fact that the asymmetry, and hence the rotational eigenfunctions, are vibrationally dependent; and (3) the fact that for all vibrations above 010, the rotational levels of like symmetry and equal J in different vibrational levels are at energies sufficiently close that the vibrational eigenfunctions are rotationally dependent, and in special cases "perturbations" lead to abnormal mixing and intensities. Only the first-named effect has been incorporated in the computations, through the method described by Benedict and Calfee (1967). Table 8 lists the constants used for each band. The footnotes to Table 8 list the sub-branches which are observed to disagree in a regular way from the results of the calculation, and which were adjusted accordingly. The lines that are exceptionally perturbed (effect 3) are identified by the symbol P following  $K'_c$ ; for these the total intensity of the two "interacting" lines was divided as required by the calculated vibrational mixing ratios or further adjusted to agree with measurements. No general statement can be made concerning the accuracy of the intensities of individual lines; for the low-J lines of the strongest bands it should be within  $\pm$  10 percent, within a factor of two for other lines of sufficient intensity (> 10<sup>-25</sup> cm<sup>-1</sup>/mol-cm<sup>-2</sup>) to appear in laboratory and/ or solar spectra, and within an order of magnitude for the weakest lines.

The intensities of the isotopic lines of species 181 and 171 were taken equal to those of 161 multiplied by the abundance factor (except for the cases of strong perturbation where the vibrational mixing ratios are different). The asymmetric isotopic species 162 is widely different, so that a completely independent calculation of its intensities, in both pure rotation and vibration-rotation has been made. The band parameters are included in Table 8.

#### 4.1.3 LINE WIDTHS

Recent high-resolution spectra of air-broadened or  $\rm N_2$ -broadened water vapor lines (Brault, 1972, private communication) have in general confirmed the calculations of Benedict and Kaplan (1959) to  $\pm$  10 percent. A striking discrepancy is, however, observed (Blum et al, 1972) for the lines of highest J which are much narrower than the lower limit of 0.032 cm  $^{-1}$  atm  $^{-1}$  which was imposed on the calculated value by choosing a minimum collision diameter equal to the kinetic-theory diameter. If the Anderson Theory (Anderson, 1949) is modified by eliminating a distance of closest approach (that is, setting the kinetic theory collision diameter equal to zero) the calculated half-width at half-height of  $^{16}$ <sub>1,16</sub>  $^{-15}$ <sub>0,15</sub> is lowered from 0.032 to 0.0098 cm  $^{-1}$ , still slightly above the observed value (0.0086). The validity of the theory is thus in question for high-J transitions but a revised

Table 8. Water Vapor Band Intensity Data and Interaction Coefficients

Vo			<b></b>	s <mark>0</mark> (296K)	R	Interaction Coefficients			
cm <sup>-1</sup>	iso	v' v"	Rot Type	cm <sup>-1</sup> /molcm <sup>-2</sup>	Debyes	α	β	Υ .	Notes
1403.489	162	010 000	A B	8.0 -022 1.92 -021	.066 .105				
1556.895	161	020 010	В	8.61 -021	.171				(1)
1588.279	181	010 000	В	2.12 -020	.121				(1)
1591.32	171	010 000	В	3.93 -021	.121				(1)
1594.736	161	010 000	В	1.061-017	.121	.025	.0065 .013	004 005	(2)
2062.318	161	100 010	В	8.9 -023	.0167				
2161.188	161	001 010	A	4.9 -022	.0394		0108	015	
2709.35	182	100 000	A	1.31 -024	.0437				
2723.687	162	100 000	A B	6.53 -022 2.0 -023	.0437 .0076	.0322 -1	.0130	.077	
2782.014	162	020 000	A B	8.1 -023 9.0 -024	.0153				
3072.058	161	030 010	В	7.99 -023	.0121				(1)
3139.02	181	020 000	В	1.32 -022	.0070				(1)
3144.96	171	020 000	В	4.92 -023	.0070				(1)
3151.631	161	020 000	В	6.58 -020	.0070	ĺ	.005	.003	(3)
3640.245	161	110 010	В	1.50 -022	.0149				(1)
3649.690	181	100 000	В	7.24 -022	.0149				(1)
3653.14	171	100 000	В	1.33 -022	.0149	ĺ			(1)
3657.054	161	100 00	В	3.62 -019	.0149	.075	.035	.028	(3)
3707.459	162	001 000	A B	1.2 -021 3.0 -022	.0509 .0255				
3736.509	161	011 010	Λ	3.30 -021	.0708				(1)
3741.571	181	001 000	A	1.60 -020	.0708				(1)
3748.36	171	001 000	A	2.96 -021	.0708				(1)
3755.924	161	001 000	A	7.994-018	.0708	.0695 .0278	.0310	.0160 .0064	(4)
4099.954	162	110 000	A B	2.0 -023 1.5 -024	.0088	(F=	1+0.15K	a)	(5)
4145.483	162	ੁ 030 000	A B	2.0 -023 1.5 -024	0	(F=	1-0.15K	a05m)	(5)
4666.720	161	030 000	В	2.0 -022	.00032	.01	.10	.12	
5089.539	162	011 000	A B	3.0 -023 6.0 -024	.0069	.02	-		
5180.36	161	120 010	В	1.47 -023	.0040				(1)
5221.28	181	110 000	В	3.66 -023	.0028				(1)
5227.75	171	110 000	В	6.77 -024	.0028				(1)
5234.981	161	110 000	В	1.83 -020	.0028	.05	015	02	
5276.776	161	021 010	A	7.45 -022	.0286				(1)
5310.43	181	011 000	A	1.81 -021	.0203				(1)
5320.25	171	011 000	A	3.36 -022	.0203				(1)
5331.245	161	011 000	A	9.06 -019	.0203		.0144	.02	

Table 8. Water Vapor Band Intensity Data and Interaction Coefficients (Contd)

٧ <sub>o</sub>	v <sub>o</sub>			s <mark>0</mark> (296K)	R	Interaction Coefficient			icients
cm <sup>-1</sup>	iso	v' v"	Rot Type	$\mathrm{cm}^{-1}/\mathrm{mol}~\mathrm{cm}^{-2}$	Dobyes	α	e	Υ	Notes
5372.114	162	200 000	A	1.2 -023	.0042				······································
6679.21	161	130 010	В	4.32 -024	.00194				
6755.40	181	120 000	В	7.05 -024	.00112				
6775.10	161	120 000	В	3.53 -021	.00112				
6779.08	161	031 010	A	6.94 -023	.0076				
6844.59	181	021 000	А	1.13 -022	.0044				
6857.32	171	021 000	А	2.09 -023	.0044				
6871.512	161	021 000	A	5.64 -020	.0044				
7186.68	181	200 000	В	1.06 -022	.0042				
7201.48	161	200 000	В	5.29 -020	.0042				
7213.26	161	111 010	А	3.98 -022	.0157				
7222.68	181	101 000	A	1.49 -021	.0157				
7235.57	171	101 000	A	2.76 -022	.0157				
7249.93	161	101 000	A	7.47 -019	.0157				
7371.79	161	012 010	В	2.17 -024	.00131				
7417.54	181	002 000	В	1.06 -023	.00131				
7430.54	171	002 000	В	1.96 -024	.00131				
7745.04	161	002 000	В	5.29 -021	.00131				
8238.84	161	041 010	A	5.88 -024	.00204				
8273.95	161	130 000	B	2.4 -022	.00027				
8341.32	181	031 000	A	7.2 -024	.00102				
8356.70	171	031 000	A	1.33 -024	.00102				
8373.82	161	031 000	A	3.6 -021	.00102				
8734.97	161	121 010	Α .	4.10 -023	.0037				
8761.57	161	210 000	В	3.6 -022	.00031				
8779.75	181	111 000	A	9.96 -023	.0037				
8792.63	171	111 000	A	1.85 -023	.0037				
8807.00	161	111 000	A	4.98 -020	.0037				
t 8966.53	181	012 000	В	2.4 -024	.00057				
9000.13	161	012 000	В	1.2 -021	.00057				
9833.58	161	041 000	A	4.8 -023	.00011				

#### Notes to Table 8.

- Insufficient data to establish interaction coefficients; these are assumed identical with corresponding band of 161.
- (2) Lower line for strong lines (L rigid>1); upper line for others.
- (3) Many lines, especially those with entranced resonance with 001, require special treatment.
- (4) Lower line for strong lines (L rigid>0.5); upper line for others.
- (5) Very close resonance of these two states at  $K_a = 0$ , all transition moment attributed to 110-0.

calculation with  $b_{min}$  = 0 does reproduce the empirical results better than the original calculation. Accordingly this has been incorporated in the current tabulation. As in previous computations, no vibrational dependence of the width has been included. The widths of the isotopic lines (181 and 171) have been set equal to those of 161; for 162 a new calculation, with  $\mu_e$  = 1.847,  $q_{air}$  = 2.62 x 10<sup>-26</sup> esu and  $b_{min}$  = 0 has been made, where  $\mu_e$  is the dipole moment of water,  $q_{air}$  is the effective quadrupole moment of the colliding gas and  $b_{min}$  is the collision diameter.

#### 4.2 Carbon Dioxide

#### 4.2.1 LINE POSITIONS

The line positions and lower-state energies of each of the significant isotopic modifications of  $CO_2$  were calculated for each band by a rotational formula for the linear molecule including terms up to  $D_vJ^2(J+1)^2$ . For some of the higher states involving Fermi resonances of high rank, an additional term  $H_vJ^3(J+1)^3$  was required. A very few of the vibrational levels are involved in a rotational perturbation, for which special calculations were needed as discussed below. The constants for each level are summarized in Table 9. For each isotopic species the band constants form a self-consistent set; that is, if a vibrational state appears more than once, as either initial or final state, its value of  $G_v$ ,  $B_v$ ,  $D_v$  (and occasionally  $H_v$ ) is the same. This requirement results in some deviations of the smoothed final line positions from their best observed values, but in general the positions of observed lines, up to J=40, will be within +0.01 cm<sup>-1</sup> of the tabulation.

The constants were calculated for each isotopic species separately, using a set of constants similar to those of Chedin and Cihla (1972), for 626, 636, and 628, but the isotopic sets were not consistently readjusted to fit a potential function. However, for isotopic forms for which the data are less extensive, approximate isotopic relations were used.

The data used for the band constants are taken from various sources. The highest precision data are those for the laser transitions 00011-10001 and 00011-10002 in the 626 isotope. The measurements of Gordon and McCubbin (1965, 1966), Oberly et al, (1968), and Drayson (1967) provide the data for interrelations among the lowest states. The most extensive data for the higher states are those from the planet Venus, as observed and summarized by Connes et al, (1969).

The vibrational notation may not be familiar to all users, and accordingly will be explained at this point. Five digits are used for each state, in order,  $v_1v_2 \ell v_3r$ . The fifth digit, r, takes the possible values 1, 2, ...  $v_1 + 1$ , and serves to locate the level in the Fermi resonating group of v + 1 levels;  $v_1, v_2 \ell$ ,  $v_3$ ;  $v_1 - 1(v_2 + 2)^{\ell}$ ,  $v_3$ ; ... 0,  $(v_2 + 2v_1)^{\ell}$ ,  $v_3$ . The value of r decreases with increasing energy. (In

Table 9. Vibrational Energy Levels and Molecular Constants for  ${\rm CO}_2$ 

Energy Level	G	B .	D Multiply	Energy Level	G	В	D Multiply	Energy Level	G	В -	D Multiply
	{cm <sup>-1</sup> }	(cm <sup>-1</sup> )	by 10 <sup>-7</sup> (cm <sup>-1</sup> )		(cm <sup>-1</sup> )	(cm <sup>-1</sup> )	by 10 <sup>-7</sup> (cm <sup>-1</sup> )		(cm <sup>-1</sup> )	(cm <sup>-1</sup> )	by 10 <sup>-7</sup> (cm <sup>-1</sup> )
	Iso	tope 626		40004	5197.249	0.390092	1.89	41114 c	1081.179	U.387643	1.56
00001	0.00	0.390218	1.331	32203 c	5245.469	.391498	1.335	41114 d		.389753	1.66
01101 c	667.379	. 390643	1.355	32203 d 21113 c	5475.071	.388153	1.535 1.61*	41113 c 41113 d	8250.644	.386233	J.355 1.355
01101 d	067.379	.391253	1.355	21113 d	3473.071	.309123	1.705	41112 c	8425.000	.386817	0.935
				40002	5475.565	.390093	0.895*	41112 d		.388517	0.965
10002	1285.412	. 390481	1.563	13312 cd	5531.279	.389732	1.52	11132 c	8803.265	. 381858	1.49
02201 c 02201 d	1335.129	.391682	1.389 1.379	05511 cd 21112 c	5627.254 5632.760	.390913	1.44 1.265	11132 d 03331 cd	8863.548	.382744	1.56 1.40
10001	1388.187	. 390188	1.142	21112 d	3432.100	.388128	1.385	· 11131 c	8944.146	.381264	1.22
				13311 cd	5730.618	.389269	1.51	11131 đ		.381874	1.18
11102 c 11102 d	1932.470	.390736	1.441	21111 c 21111 d	5790.579	.387413	1.125 1.025	20033	9388.990	.38234	1.71
03301 cd	2003.238	.392420	1.403	10022	5915.209	.388613 .384528	1.625	12232 c	9419.189	.38234	1.71
11101 c	2076.865	.390416	1.281	02221 c	5958.539	.385617	1.35	12232 d	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,		1.25
11101 d		.391344	1.195	02221 d			1.31	26032	9516.970	.38048	1.39
00011	2349.146	.387140	1.325	10021	6016.690	.383917	1.17	12231 c 12231 d	9589.929	.38247	1.43 1.53
20003	2548.280	. 391183	1.76	30014	6075.983	.386896	2.052	20031	9631.350	.38125	1.04
12202 c	2585.006	. 391843	1.45	22213 c	6103.670	.389428	1.29				
12202 d	2471 113	200116	1.25	22213 d	(17/ (22	300405	1:67	21133 c	9947.48	. 38251	1.55
20002 04401 cd	2671.113 2671.690	.389556	1.331 1.42	14412 c 41102 c	6176.623 6179.010	.390485	1.54 1.33	21133 d 21132 :	10145.43	.38351 .38096	1.63
12201 c	2760.735	. 391535	1.44	30013	6227.924	.386697	1,643	21132 d		.38258	1.35
12201 d			1.25	22212 c	6288.492	.388472	1.38	21131 c	10297.05	.38127	1.10
20001 01111 c	2797.154 3004.016	.390563	0.985 1.349	22212 d 30012	6347.854	.386451	1.28 0.951	21131 d	Isotope	. 38237	1.00
01111 d	3004.016	. 388190	1.349	41101 c	6388.085	.390290	0.93	00001	0.00	.390235	1.330
				14411 cd	6398.047	.390017	1.37				
21103 c	3181.450	.391028	1.63	22211 c	6474.530	. 388662	1.53	01101 c	648.484	.390598	1.330
21103 d 13302 cd	3240.564	,392316 .392696	1.75 1.51	22211 d 30011	6503.081	.387974	1,21 0,719	C]101 d		.391236	1.330
21102 c	3339.340	.390035	1.37	11122 c	6537.958	.384804	1.475	10002	1265.820	.390920	1.58
21102 d		.391145	1.37	11122 🖪		.385722	1.606	02202 c	1297.269	.391603	1.274
05501 cd 13301 ca	3340.475 3442.256	.393908	1.44 1.35	11121 c 11121 d	6679.709	.384310	1.216 1.115	02202 d 10001	1370.067	.389707	1.334
21101 c	3500.590	.390461	1.14	00031	6972.578	.385127 .380990	1.331	10001	13/0.06/	.307/07	1.160
21101 d		.391700	1.01					01102 c	1896.49	.391137	1.48
10012	3612.844	. 387496	1.57	31114 c	6688.274	. 388547	1.735	01102 d		. 392096	1.13
02211 c 02211 d	3659.277	.388647	1.383 1.373	31114 d 31113 c	6863.553	.390246 .386930	1.825	03301 cd 11101 c	1946.343	.392293 .390015	1.34
10011	3714.781	.387051	1.13	31113 d	00031333	.388333	1.485	11101 d	2000	.390975	1.13
				31112 c	7023.672	.386755	1.19	00011	2283.490	.387300	1.325
30004 22203 c	3792.702 3821.984	.391760	2.02 1.46	31112 d 20023	7133.819	.388127 .385288	1.165	20003	2507.50	.391815	1.76
22203 d	3521.764	. 372333	1.68	12222 c	7166.049	.386017	1.15	12202 c	2531.63	.39220	1.22
14402 cd	3898.117	. 393434	1.54	12222 d			1.35	12202 d			1.40
30003 22202 e	3942.492 4007.850	.389584	1,66 1. <b>4</b> 7	31111 c 31111 d	7203.814	.387607	1.05 0.85	04401 cd 20002	2595.614 2645.086	.392987 .389826	1.34
22202 d	40071830	.332403	1.40	12221 c	7338.149	.385487	1.33	12201 c	2700.25	.39126	1.30
30002	4063.908	. 389606	0.935	12221 d			1.28	12201 đ			1.34
14401 22201 c	4122.347 4197.413	.393036	1.36	20021	7377.679 7602.529	.384403	1.45 1.315	20001 01111 c	2750.48 2920.244	.389670	0.91 1.325
22201 d	4197.413	.391719	1.63 1.13	01131 c 01131 d	7602.329	.381503	1.355	01111 d	2920.244	.387664 .389286	1.325
30001	4225.110	.391090	0.521								
11112 c 11112 d	4247.713	.387773	1.49	40015	7283.981	.389550	2.31	21103 c 21103 d	3127.28	.39155	1.70
03311 cd	4314.913	.388690 .389387	1.56 1.405	32214 c 32214 d	7307.651	.389942	1.03	13302 cd	3169.21	.39308	1.6E 1.45
11111 c	4390.628	. 387350		40014	7460.530	.387322	1.93	21102 c	3289.71	.39001	1.25
11111 d	4673 337	. 388230	1.17	32213 c	7505.219	.388632	1.23	21102 d	2261 57	.39120	1.25
00021	4673.327	. 384063	1.319	32213 d 40013	7593.690	. 385562	1.34 1.04	13301 cd 21101 c	2433.70	.39188 .39292	1.25 1.04
31104 c	4416.150	.391357	1.63	32212 c	7694,416	.388252		21101 d			1.10
31104 d		.393078		32212 đ			1.14	10012	3527.740	.388030	1.56
31103 c 31103 d	4591.118	. 389925 . 391348		40012 21123 c	7734.452 7743.700	.386954 .385358	0.59 1.25	02211 c 02211 d	3557.314	.388668	1.28 1.33
33102 c	4753.450	.389708		21123 d	7743.700	. 386488	1.73	10011	3632.917	. 386726	1.21
31102 d		.391098	1.33	32211 c	7897.573	. 388965	1.33*				
20013	4853.620	.388188		32211 d	7001 470	204000	0.939**	30001	4145.95	.39010	1.22*
12212 c 12212 d	4887.970	. 388958	1.33	21122 c 21122 d	7901.479	.384008	1.31*	11112 c 11112 d	4147.234	.38811 .38915	1.49* 1.59
31101 c	4938.410	.389358		40011	7920.840	.388558	0.60		4194.704	,38934B	1.33
31101 d	1000	.391130		21121 c	8056.024	.384408	1.11	11111 c	4287.695	.387654	1.27
04411 cd 20012	4970.909 4977.830	.390148 .386529		21121 d 10032	8192.556	.385525	1.08 1.56	11111 d 00021	4543.552	.387977 .384360	1.26 1.33
12211 c	5061.776	.388508		02231 c	8332.880	.382600	1.30			,554500	.,
12211 d			1.12	02231 d			1.28	20013	4748.058	.388845	1.815
20011 01121 c	5099.660 5315.730	.387448		1003	R293.957	.380805	1.13	12212 c 12212 d	4770.985	. 38925	1.25 1.27
01121 d	JJ1 J. / 3U	.384548		*,** J-d	ependent in	teractions		04411 cd	4831.99	.39003	1.34

Table 9. Vibrational Energy Levels and Molecular Constants for  ${\rm CO}_2^{\times}$  (Contd)

Energy Level	G .	В	D Multiply	Energy Level	G	В	D Multiply	Energy Level	G	В	B Multiply
	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )	by 10 <sup>-7</sup> (cm <sup>-1</sup> )		(cm <sup>-1</sup> )	(cm <sup>-1</sup> )	by 10 <sup>-7</sup> (cm <sup>-1</sup> )		(cm <sup>-1</sup> )	(cm <sup>-1</sup> )	by 10 <sup>-7</sup> (cm <sup>-1</sup> )
	(6111)	, c.m /	(Ca) /		· · · · ·	· · · · · · · · · · · · · · · · · · ·	(611)		· · · · · ·	· · ·	
20012	4887.390	0.386847	1.47	21102 d	3281.07	0.36916	1.12	11112	4223.33	0.37616	1.31
12211 c	4938.80	.38831	1.44	13301 cd	3404.93	. 37077	1.28	11112 d		.37700	1.34
12211 d			1.40	21101 c	3453.99	.36881	0.98	11111 c	4367.08	.37600	1.18
20011	4991.350	.386705	0.94	21101 d		.37007	0.90	11111 d		.37686	1.15
01121 c	5168.600	. 384695	1.33	10012	3571.143	. 365284	1.27	00021	4655.205	.372674	1.20
01121 d		. 385305	1.33	02211 c	3632.52	. 366595	1.19	20013	4821.500	.376411	1.62
21113 c	5357.004	.388614	1.50	d 10011	2675 120	365534	1.15	20012	4939.350	.375131	1.21
21113 d	3337.004	.390108	1.68	10011	3675.130	.365524	0.95	20011 21112 c	5064.910 5593.645	.376321 .375625	1.00
13312 ed	5397.09	.38978	1.30	30003	3856.657	.367405	1.24	21112 d	33331043	.376759	1.22
21112 c	5519.944	.387038	1.16	30002	3987.610	. 368174	0.91	00031	6945.610	.369691	1.20
21112 d		.388206	1.30	11112 c	4201.19	.365666	1.23		Isotop	e 638	
13311 cd	5588.17	.38907	1.44	11112 d		.366423	1.28	00001	0.00	.368180	1.11
21111 c	5662.269	.386837	1.10	03311 cd	4283.35	.36726	1.19				
21111 d		.387936	1.00	11111 c	4346.13	.365716	1.05	01101 c	643.23	. 36857	1.12
				11111 d		. 366568	1.00	01101 d		.36912	1.12
30014	5951 600	.389640	2.326	00021	4639.502	.362372	1.11				
22213 c	5970.949	. 389913	1.57	20013	4791.260	.365734	1,50	10002	1244.93	.36820	1.30
12213 d	6110 515	303546	1.33	12212 c	4836.63	.366707	1.25	02201 c	1286.86	.36951	1.14
0013	6119.618	.387540	1.786	d	4004 055	30.00	1.27	02201 d			1.11
2212 c	6155.37	.38852	1.36	20012	4904.850	.364844	1.11	10001	1342.37	. 36844	0.90
2212 d 0012	6241.964	185050	1.30	12211 c	5012.\$5	. 366735	1.26	00011	2265.973	. 365388	1.11
2211 c	6326.049	.385859 .388103	1.113	20011	5042.570	.366124	1.06 0.86	20002 c 01111 c	2588.43	.36778	1.04
2211 d	0320.049	. 200103	1.35	01121 c	5277.147	.362848	1.06	01111 c	2897.58	.36579	1.12
0011	6363.616	. 387033	0.906	d d		.363356	1.06	10012	3490.39	.36633 .36588	1.12
11122 c	6374.497	.38521	1.46	21113 c	5406.06B	.365893	1.41	02211 c	3529.59	.36671	1.14
1122 d	03/4/4//	.38607	1.56	a	3400.000	.366904	1.31	02211 d	3323.33	.30071	1.12
0031	6780.215	.381353	1.33	21112 c	5558.553	.365318	1.10	10011	3587.54	.36525	1.01
				ď	-3201321	. 366240	1.10	00021	4508.749	.36260	1.11
1114 c	6552.954	. 388958	1.63	21111 c	5727.048	.365948	1.11	20012	4814.570	.364810	1.11
1114 d		. 390896	1.83	d		.367138	0.81	20022	Isotop		****
1113 c	6736.694	. 387368	1.63	10022	5858.022	.362490	1.357	00001	0.00	.378658	1.21
1113 đ		.388906	1.58	02221 c	5915.23	.36376	1.18	01101 c	645.72	.379036	1.22
11112 c	6892.054	.386378	1.33	ď			1.15	01101 d		.379627	1.22
11112 u		.387706	1.18	10021	5959.594	.362605	0.896	10002	1254.83	.37900	1.40
31111 c	7046.029	.386858	1.23	30014	5 <del>9</del> 93.581	.366337	1.78	02201 c	1292,80	.38000	1.22
31111 d		.388236	0.93	30013	6127.782	. 364495	1.31	02201 đ			1.22
1131 c	7393.599	.381803	1.33	30012	6254.592	.365274	0.80	10001	1355.52	.37849	1.04
1131 d		. 382391	1.33	30011	6429.172	.366616	0.60	00011	2274.33	. 37579	1.21
	7101 610	******		00031	6922.210	.359479	1.10	01111 c	2918.38	.37617	1.22
10013	7481.510	.385435	0.33	10000				01111 d		.37675	1.22
40012 10032	7600.130 7981.180	.385855	0.63	10032	8120.104	.359684	1.25	10002	3508.07	.37641	1.41
10032	8089.040	.382275	1.52 1.26	10031	8220.363	.359656	0.95	10001	3609.05	.37540	1.11
	Isotop		1,20	00001	0.00	.378641	1.205	00001	0.00	.346799	1.04
00001	0.00	.368164	1.11	00002	0.00	.570041	1.105	01101 c	657.33	.347224	1.04
				01101 c	664.735	. 379065	1.22	01101 d	037.33	.347736	1.04
01101 c	662.368	.368588	1.13	01101 d		.379639	1.22	10002	1230.20	.34620	
1101 d		.369128	1.13					02201 c	1315.08	.34812	1.10
				10002	1271.875	.378738	1.40	02201 d			1.04
0002	1259.430	.368114	1.26	02201 c	1329.87	.380061	1.24	10001	1347.22	.34776	
2201 c	1325.15	.369520	1.20	02201 d			1.22	00011	2313.97	.34412	1.04
2201 d		_	1.16	10001	1376.28	.378806	1.04	01111 c	2959.06	.34455	1.04
10001	1365.845	.368502	02962					01111 d	•	.34504	1.04
				11102 c	1916.31	. 37903	1.27	10002	3525.205	.343840	1.16
1102 c	1901.748	.36845	1.23	11102 d		.37989	1.32	10001	3638.067	.344636	0.907
11102 d	1000 200	.36925	1.28		1995.36	.37977	1.22		Isotope		
3301 cd	1988.328	.370182	1.20	11101 c	2052.41	.37894	1.15	00001	0.00	. 35695	1.07
11101 c	2049.346	.36860	1.06	11101 d	2242 **	.37987	1.10	01101 ¢	659.70	. 35737	1.08
1101 d	2222 112	. 36954	1.01	00011	2340.01	.375659	1.20	01101 d	2222	.35789	1.08
00011	2332.112	. 365267	1.11	20002	2522 50	37004		00011	2322.52	.35419	1.07
10003	2500.776	160467	1.44	20003	2523.58	. 37924	1.60				
2202 c	2549.425	.368463 .36954	1.44	12202 c 12202 d	2566.33	.380125	1.35 1.25				
12202 d		• 20724	1.27	20002	2641.26	-37814	1.18				
20002	2614.235	.367807	1.04	12201 c	2743.68	.38005	1.18				
04401 cd	2651.875	.37085	1.22	12201 d	2/43.00	. 38003	1.23				
2201 c	2728,264	.36966	1.30	20001	2776.00	.37927	0.88				
2201 d	2.25,204	120700	1.07	01111 c	2992.310	.376103	1.22				
20001	2757.229	.369039	0.77	01111 d	2992.310	.376664	1.22				
01111 c	2982.106	.365707	1.13	10012	3590.86	. 375835	1.38				
				02211 c	3645.02	.377091	1.24				
21103 c	3127.31	. 36855	1.34	02211 d	20.4.00		1.22				
21103 d	<b></b>	. 36957	1.43	10011	3693.64	. 375754	1.06				
13302 cd	3200.15	.37023	1.28								
21102 c	3281.07	.36817	1.14								

this scheme,  $v_2$  is always equal to  $\ell$ .) The desirability of labelling the states in Fermi resonance by the same symbols except for r is to emphasize the very important role played by the Fermi resonance, which is very nearly exact for most of the groups. It must also be emphasized very strongly that the long-established custom of calling the upper level of the  $(10^00, 02^00)$  resonance at 1388.18 cm<sup>-1</sup>,  $v_1$ , and the lower level at 1285.41,  $2v_2$ , is not only confusing the issue, but is wrong, since the now ten year old work of Amat and Pindert (1965) has shown that the unperturbed position of  $2v_2^0$  lies above that of  $v_1^0$ , in the 626 isotope. This is also true in 627, 628, and 828, but in 636, 637, 638, it lies below. It seems vastly preferable always to label the upper level 10001 and the lower 10002.

#### 4.2.2 LINE INTENSITIES

The intensity data (summarized in Table 10) are based on quantitative studies of resolved lines where such exist; and where not, on total intensities in a given region. The relations between the strengths of the principal band in a region and its associated weaker "hot" and isotopic neighbors were based on computations relating the transition moments to the vibrational eigenfunctions, taking into account terms up to the quartic in the molecular constants, with particular attention to the degree of Fermi mixing in the states, and an approximate calculation of the "unperturbed" (before Fermi mixing) transition moments. This procedure appears to give fairly good agreement for the ground-state and "first-hot" transitions in such Fermi groups as 2001-0000 and 3001-0000, and seems adequate for estimating strengths of higher unobserved hot bands. However, when experimental data are available (Burch, 1970), as for the 12201-11102 band at 828.28 cm<sup>-1</sup>, these were used.

For the isotopic molecules, empirical data were again used where available, as for 628 bands which are forbidden in the symmetric molecules. When the isotopic bands overlap stronger bands of 626, the abundance ratios were used to estimate the total strength of a group, but the particular Fermi parameters were used to divide the strengths.

The influences of vibration-rotation interactions on line intensities has been measured in some cases. As a generalization, it can be said that these are usually negligible for the parallel bands ( $\ell' - \ell'' = 0$ ) but become of considerable importance for all the perpendicular bands ( $\ell' - \ell'' = \pm 1$ ) except those in the 15  $\mu$ m region. For all the other bands, Coriolis-type resonances are responsible for inducing a large part of the transition moment in the R- and P-branches, thus "borrowing" intensity from the stronger parallel bands, while leaving the Q-branches unchanged. Accordingly, the latter may remain very weak (or in some cases be unobservable - for example, the 410 group). We have used the approximate equation  $S_m = S_0^0$  (1 + m  $\xi_v$ ) to correct for this interaction, with the values

Table 10. Band Origins and Intensities for  ${\rm CO_2}$ 

Band Center	Upper Level	Lover Level	Iso- tope	SV at 296K (multiply by	Band Center	Upper Level	Lower Level	Iso- tope	SV at 296K (multiply by
(cm <sup>-1</sup> )				10 <sup>-22</sup> mo1 <sup>-1</sup> cm <sup>2</sup> cm <sup>-1</sup> ) jr	(cm <sup>-1</sup> )				10 <sup>-22</sup> mo1 <sup>-1</sup> cm <sup>2</sup> cm <sup>-1</sup> )
471.415	20003	11101	626	0.0087	681.27	12201	11101	627	.0082 2
479.829	13302	12201	626	.0012	681.521	13301	12201	626	.460
494.537 508.141	12202 12202	11101	636	.00079 Q	683.501	11101	10001	628	.77
510.337	21103	11101 20002	626 626	.0516 .0040	683.870 686.13	12201 11101	11101 10001	626 627	9.05 0.13
526.423	11102	10001	636	.035	688.678	11101	10001	626	148.8
535.903	11102	10001	628	.0011 Q	696.823	22201	21101	626	0.0195
542.186 544.283	21102 11102	20001 10001	626 626	.00711 2.723	699.14	10001	01101	638	.058
548.275	13302	04401	628	0.00026 Q	703.477	10001 21101	01101 20001	628 626	8.20 0.246
557.742	14402	05501	626	.00253	707.883	20001	11101	628	.024
561.097 564.889	12202 20002	03301	628	.0058	709.80	10001	01101	637	.0094
568.874	13302	11101 04401	628 626	.0716	710.765	10011	01111 01101	626 627	.0202 1.26
570.87	12202	03301	627	.00092 Q	71.2.487	20002	11102	628	0.013
573.536	13302	04401	636	.00115	713.387	20001	11101	636	.047
576.598 578.605	11102 21102	02201 12201	628 626	.169 .0376	713.59	20001	11101	627	.0038 4.784
578.85	20002	11101	627	.00072 Q	720.289 720.808	20001 10001	11101	626 626	1853.
580.424	22203	13302	626	.0096	721.583	10001	01101	636	17.9
581.768	12202	03301	626	1.934	724.196	11101	02201	628	0.315
585.287 586.44	12202 11102	03301 02201	636 627	.034 .0439	724.95	20002	11102	627	.0024 Q
589.46	21102	12201	636	.00055 Q	732.54 733.45	11101 21101	02201 20001	627 636	.0474 .0021 Q
594.248	20002	11101	626	.908	738.643	20002	11102	626	3.021
595.65	21103	12202	636	.0038	739.824	11101	02201	636	0.70
596.444 597.062	21103 10002	12202 01101	626 628	.257 5.19	739.936 739.855	12201 21101	03301 12201	628 626	.0157 .176
597.341	11102	02201	626	52.08	741.736	11101	02201	626	79.01
599.028	20003	11102	628	0.021	747.32	12201	03301	627	0.0025 Q
599.221	11102	03201	636	.702	748.546	20002	11102	636	.0378
601.70 607.14	10002 10002	01101 01101	638 627	.055 1.17	753.055 754.334	13301 21102	04401 12202	628 626	.00058 Q .1607
607.27	20003	11102	628	0.021	757.497	12201	03301	626	3.288
607.993	20002	11101	636	.0111	765.896	13301	04401	636	0.00173 Q
608.828	10012	01111	626	.0175	770.355	13301	04401 10002	626 636	.1351
609.11 611.01	10002 20003	01111	637 636	.0106 .102	771.273 781.872	11101 14401	05501	626	.0051
615.810	20003	11102	626	6.89	789.916	11101	10002	628	.0056
617.336	10002	01101	636	20.5	790.536	11101	10002	627	.0010 C .0548
618.033	10002 21103	01101 20003	626 636	1436. 0.0085	791.060 791.452	21102 11101	20003 10002	626 626	11.23
619.78 633.170	21103	20003	626	.649	803.76	12201	11102	636	0.0052
636.754	01111	00011	636	.0121	826.516	12201	11102	628	.0009 Q
637.58	13302	12202	636	.013	828.265 829.467	12201 21101	11102 20003	626 626	.201 .0548
640.670 642.318	11102 11102	10002 10002	636 628	2.60 0.78	857.250	13301	12202	626	.0110
643.23	01101	00001	638	3.57	864.684	20001	11102	626	.0432
644.435	11102	10002	627	0.15	883.151	01111	11101	636	.00495 .0132
645.72 646.11	01101 02201	00001 01101	637 637	.642 .055	998.542 913.423	02211 00011	12201 10001	626 636	.0614
647.058	11102	10002	626	. 222	915.584	21101	12202	626	.00195 Q
648.484	01101	00001	636	860.	917.627	10011	20001	626	.0087
648.785	02201	01101	636	73.4	927.151	01111	11101	626 628	.3556 .00135
649.074 649.331	03301 04401	02201 03301	636 636	4.69 0.266	932.760 941.731	01111	11101 20002	626	.01146
649.580	05501	04401	636	.0142	952.310	21101	20003	626	.00064 Q
650.02	12202	11102	627	.0118	960.959	00011	10001	626	4.910
652.536	12202	11102	626	16.52	963.73 966.267	00011	10001 10001	627 628	.0032 .0195
654.870 655.558	01111 13302	00011 12202	₹ 626 626	0.885 0.990	1017.670	00011	10002	636	.0726
657.33	01101	00001	828	.343	1023.744	01111	11102	636	.00072
657.69	02202	00111	828	.0277	1063.734	00011	10002	626 627	6.324 .0047
657.553 659.79	14402 01101	13302 00001	626 728	.0442	1068.135 1071.546	00011 01111	10002 11102	626	.540
661.32	13301	12201	636	.0055	1072.682	00011	10002	628	-0285
662.368	01101	00001	628	330.	1074.271	02211	12202	626	.0227
662.782	02201	01101	628	26.2	1080.358	01111	11102	628	.00243
663.157 663.178	12201 03301	11101 02201	636 628	0.106 1.50	1239.380	11102	01101	628	0.0351
663.547	04401	03301	628	0.078	1244.93	10002	00001	638	.0038
664.735	01101	00001	627	62.2	1259.430	10002	00001	628	.382 .0220
665.135	02201	01101	627 627	4.88 0.285	1271.875	10002 10001	00001 00001	627 638	.0220
665.49 667.026	03301 11101	02201 10001	636	1.58	1365.845	10001	10000	628	.561
667.379	01101	00001	626	82580.	1376.28	10001	00001	627	.0323
667.750	02201	01101	626	6488.	1386.978	11101	01101	658	.0516
668.109 668.227	03301 21102	02201 20002	626 626	382.4 0.312	1846.321	21101	05501	626	.0003315
668.452	04401	03301	626	18.45	1859.02	20003	01101	636	.0001615
668.785	05501	04401	626	0.976	1860.232	30004	11102	626 626	.0000012
669.106	06601 12201	05501 11101	626 628	.077 .060	1865.607	30003 20003	11101 01101	656	.015620

Table 10. Band Origins and Intensities for  ${\rm CO_2}$  (Contd)

2245.17         10011         10001         638         .0555         3154.605         22203         0101         626         .00074           2248.356         01021         01002         638         .0816         3181.45         21103         00001         626         .00087           2248.356         03311         03301         636         1.52         3281.07         2102         00001         628         .00017           2250.60°         11111         1110         b36         0.96         3281.07         2102         00001         636         .00017           2250.7°         11111         1110         636         1.91         3139.340         21102         00001         636         .0417           2251.21         02211         02201         637         0.0264         3140.41         22202         01101         626         .0063           2253.24         10012         10002         637         0.098         3198.206         2111         1110         626         .00413           2250.045         02211         02201         636         34.6         3450.751         2111         1110         626         .00413           2260.045         020	Band Center	Upper Level	Lower Level	Iso- tope	SV at 296K (multiply by	Hand Center	Upper Level	Level	Iso- tope	SV at 290x (multiply by
1883-144   12302   01101   636   0.00149  06   2297-445   11112   11102   638   0.466   1.17   1883-144   123101   10101   636  0014  06   2297-445   12111   12201   648   0.11   1884-6.08   21012   10001   636  0014  06   2201-315   01111   01101   828   0.11   1884-6.08   21013   10002   636  0014  06   2201-315   01111   01101   828   0.11   1884-6.08   2101   19002   636  0014  06   2201-315   01111   01101   828   0.11   1884-6.08   2101-315   02001   636  0014  0014  0014						l .				
1989, 513   2220   1110   656   6016   614   7.06   2011   2011   1221   1220   626   6.019   1886, 618   1110   00001   626   626   6.019   7.06   2011   0011   627   626   6.019   7.06   7.07	(cm <sup>-1</sup> )			<del> </del>	cm cm () }	(cm <sup>-1</sup> )			·	rp² cp²¹, '}
1896_408   11102	1983.146		01101	636	0.0014906					
1986.018   21103   10000   676   10110   -07   21001.909   10021   10011   676   0.0789   10021   10011   676   0.0789   10021   10011   676   0.0789   10021   10011   676   0.0789   10021   10011   676   0.0789   10021										
1901.748   1102   00001   628   10276   0.66   2307.346   10021   2003   626   1.766   0.671   10001   626   1.766   0.66   2307.370   20011   20000   626   2.399.481   10011   626   1.0001   1.0001   626   1.0001   1.0001   626   1.0001   1.0001   626   1.0001   1.0001   626   1.0001   1.0001   626   1.0001   1.0001   626   1.0001   1.0001   626   1.0001   1.0001   626   1.0001   1.0001   626   1.0001   1.0001   628   1.0001   1.0001   628   1.0001   1.0001   628   1.0001   1.0001   628   1.0001   1.0001   628   1.0001   1.0001   628   1.0001   1.0001   628   1.0001   1.0001   626   1.0001   1										
1905.415   13102   02201   626										
1919.985   22202   11101   626   4.097   -0.66   2307.70   2311   2321   02201   628   6.097   1919.1913   21102   10001   626   4.097   -0.66   2307.71   02211   02201   628   0.097   1919.1913   21102   10001   626   6.097   -0.66   2307.71   02011   02011   626   6.097   1919.1913   21102   02002   01101   636   6.0011   -0.04   0.0011   0.001   626   6.0011   -0.04   0.0011   0.001   626   7.29   0.0012   0.0012   0.0012   0.0012   0.0012   0.0012   0.0012   0.0012   0.0012   0.0012   0.0012   0.0013   0.0013   0.0010   0.0010   0.0012   0.	1905.435									
1912.470   11102   00001   626										
1993.153   21102   10001   626										
1000.7.74   2000.2   01101   626   .00018  01   .2111.675   02111   0310   0300   626   7.29   .2210.022   2000.022	1951.153									
2004_111   21102   02201   626										
2010.022   20000   11102   626   .00011   .055   .2311.715   01121   01111   626   .1.799   .2010.030   .2010.03										7.29
2049.146										
2055.846 12201 01101 02001 628 .0.05203 2115.15 02112 02202 627 1.91 02062.41 11101 00001 627 .0.052 .0.051 2115.243 11112 11102 626 17.11 0205.80 11101 0001 627 0.055 0.055 0.056 0.065 0.068 0.0										
2007.										
2075, 380 2220; 11101 docc 626068504 21756 10011 10001 627 0809 10076, 865 11101 docc 626 1.958018 2115.7.60 10011 10001 627 0059 127						2315.243	11112	11102	626	17.11
2091.156   12201   01101   628   1.958   -0.08   2319.738   01111   01101   628   258   2594.861   20001   01101   628   0.0055   -0.05   2312.625   00011   00001   626   0.055   -0.05   2312.625   00011   00001   626   0.069   -0.055   2312.4182   00021   00011   626   20.98   0.0051   2312.1481   00021   00011   626   0.069   -0.055   2312.4182   00021   00001   626   0.069   -0.055   2312.4182   00021   00001   626   0.069   -0.055   2312.4182   00021   00001   626   1193.   1	2075.380	22202	11102	626	.008504					
2094.661   20001   01101   628   0.0055  04   2322.52   00011   00001   728   1.35   1.3										
2107.127   13001   02201   626   .253  015   2324.182   00021   00011   626   20.98	2101.996	20001	01101	636	.014903	2324.148	02211	02201		
2119-119					.253035					
1217.215   1217   1216   626   .00149   .00149   .00141   .0011   627   49.7   .00121   .0012   .001										
2198.775   20001   01101   626   0.0595   -10   2340.01   00011   00001   627   63	2120.548	22201	11101		.011904	2327.575	01111	01101	627	49.7
2148-245   30001   11101   626   0.0595   -1.0   2340-0.0   0.0011   0.0001   626   6375-0.0   6315-0.0   6315-0.0   6315-0.0   63215-0.										
2157.673   10012   10001   636   .0152   .0155   .0156   .0156   .0151   .0151   .0152   .0156   .0152   .0156   .0157   .0151   .0152   .0156   .0157   .0151   .0152   .0152   .0156   .0157   .0151   .0152   .0152   .0152   .0152   .0152   .0152   .0154   .0152   .0152   .0152   .0152   .0152   .0152   .0152   .0154   .0152   .0152   .0152   .0152   .0152   .0152   .0152   .0154   .0152   .0152   .0152   .0152   .0152   .0152   .0152   .0154   .0152   .01										
2170.488						2349.146	00011	00001	626	959800.
2180.676   20012   20001   626   .00092   .2428.547   20011   20002   626   .00146   .2429.159   .2429.159   .20011   .20002   .626   .1.059   .22214.647   .20011   .20002   .626   .1.059   .22214.647   .20011   .20002   .626   .1.059   .2224.647   .20011   .20002   .626   .1.059   .2224.647   .20011   .20002   .626   .1.059   .2224.647   .20011   .20002   .626   .1.059   .2224.647   .20011   .20002   .626   .1.059   .22224.647   .20011   .20002   .2003   .2003   .626   .0.058   .22227.88   .11111   .11102   .626   .0.058   .22227.88   .11111   .11102   .626   .0.058   .22227.88   .11111   .11102   .626   .0.058   .22227.88   .11111   .11102   .626   .0.058   .22227.88   .11111   .11102   .626   .0.058   .22227.88   .11111   .20002   .2224.647   .20011   .20003   .20003   .20003   .20003   .22227.84   .21112   .21102   .636   .0.0488   .2523.58   .20003   .20003   .628   .186   .0.0222   .2224.656   .04411   .04401   .636   .0.632   .2614.255   .20002   .20003   .628   .186   .22240.558   .20013   .20003   .636   .0.0234   .22240.558   .20013   .20003   .636   .0.0234   .22240.558   .20013   .20003   .636   .0.0234   .22240.648   .20011   .20001   .636   .0.024   .22240.648   .20011   .20001   .636   .0.0224   .2754.029   .20001   .20001   .636   .0.0224   .2754.029   .2754.029   .20001   .20001   .626   .0.0024   .2242.736   .20012   .20002   .636   .0.0234   .2244.736   .20013   .20001   .20001   .638   .0.0124   .2244.736   .20013   .20001				826	.059505					
2181.507   20013   20002   626   .00172   2429,369   10011   10002   626   .0.059   .2222.225.05   20012   20003   626   .0.00256   .2222.225.05   .20012   10001   628   .0.0558   .2225.05   .20012   .20003   626   .0.00256   .2222.525.05   .20012   .20003   .20012   .20003   .20012   .20003   .20012   .20003   .20012   .20003   .20012   .20003   .20012   .20003   .20012   .20003   .20012   .20003   .20012   .20003   .20012   .20003   .20012   .20003   .20012   .20003   .20012   .20003   .20012   .20003   .20012   .20003   .20012   .20003   .20										
2209, 298   10012   10001   628   .00558   2229, 550   20012   20003   626   .0025										
2227. 85   05511   05500   636   0.00261   2464.942   21103   01101   628   .0058   2227.784   21113   21103   636   .00488   2523.58   20003   00001   638   .0075   0220.2244   21112   21102   636   .00488   2523.58   20003   00001   638   .0020   0220.2244   21112   21102   636   .00216   2580.734   20003   00001   638   .0020   0220.2245   00021   0220.2245   00021   0220.2245   00021   0220.2245   00021   0220   0220   02001   628   .186   0220.2245   02	2205.298	10012	10001		.00558					
2227.88   13312   13302   636   .00401   .2500.776   .20003   .00001   628   .075   .2229.724   .21113   .21103   636   .00408   .2521.58   .20003   .00001   627   .0060   .2230.234   .21112   .21102   .636   .00216   .2588.43   .20003   .00001   .628   .186   .2232.93.55   .2212   .21201   .2201   .636   .00812   .2614.235   .20003   .00001   .628   .186   .2239.55   .2212   .2200   .636   .0184   .2618.702   .21102   .01101   .628   .0148   .2239.555   .2212   .2200   .636   .129   .2661.26   .20002   .00001   .628   .022   .2240.687   .20013   .20001   .636   .0.036   .0.022   .2776.00   .20001   .20001   .636   .0.028   .2797.76   .20013   .20001   .20001   .636   .0.029   .2797.602   .20001   .20001   .636   .0.029   .2242.696   .20012   .20002   .636   .0.029   .2242.796   .20012   .20002   .636   .0.029   .2797.602   .20001   .20001   .628   .0.023   .2242.696   .20012   .20002   .20002   .2342.696   .00012   .2242.796   .00011   .20001   .638   .0.0124   .2242.796   .00011   .20001   .638   .0.0124   .2242.797   .20011   .20011   .2001   .638   .0.0124   .2245.46   .0012   .2002   .638   .0.088   .0.0887   .2248.361   .0012   .2002   .2348.361   .0.0012   .2248.361   .0.0012   .2248.361   .0.0012   .2248.361   .0.0012   .2248.361   .0.0012   .2248.361   .0.0012   .2248.361   .0.0012   .2248.361   .0.0012   .2248.361   .0.0012   .2250.600   .1111   .11101   .636   .0.960   .3259.71   .21102   .20001   .626   .0.0012   .2250.600   .1111   .11102   .636   .0.96   .3289.71   .21102   .00001   .626   .0.0012   .2250.600   .										
2229.724 21113 21103 636 .00488 2523.58 20003 00001 627 .00660 2220.214 21112 21102 636 .00216 288.43 20003 00001 628 .186 .0020 2226.696 04411 04401 636 .0632 2614.235 20002 00001 628 .186 .2279.355 12212 12202 636 .129 .2641.26 20002 00001 628 .186 .2279.355 12212 12202 636 .129 .2641.26 20002 00001 628 .022 .2240.697 20011 20001 636 .0122 .2767.600 20001 00001 627 .018 .2240.697 20011 20001 636 .0122 .2767.600 20001 00001 627 .0023 .2242.096 20012 20002 636 .0258 .2791.602 20101 0101 628 .0015 .2242.776 00021 00011 638 .00124 .2242.773 02211 02201 638 .149 .3125.321 30004 01101 626 .00024 .2245.17 10011 10001 638 .0816 .3181.45 .2110 01101 626 .00024 .2246.8156 01120 11111 616 .0.980 .3258 .3261.07 .2110 00001 626 .000687 .2248.356 01120 1111 616 .0.980 .3259.1111 1110 626 .00017 .3280 .3281.07 .21102 00001 628 .00017 .2250.607 11111 1110 636 0.96 .3280 .3281.07 .21102 00001 626 .00068 .00017 .2250.607 11111 1110 636 0.96 .3280 .3281.07 .21102 00001 626 .00062 .2250.774 11112 11102 636 1.91 .3319.340 .21102 00001 626 .00063 .2251.35 10011 10002 637 .0.0264 .3340.471 .2220 01101 626 .00017 .2251.00 .0221 .02201 .02201 .0370 .0.046 .3360.529 .30002 .01101 626 .00063 .2251.35 10011 10001 637 .0.098 .3398.206 .2111 1110 1101 636 .0.042 .2251.35 10011 10001 637 .0.098 .3398.206 .2111 1110 1101 636 .0.042 .2251.35 10011 10001 637 .0.098 .3398.206 .2111 1110 1101 636 .0.0042 .2251.35 10011 10001 637 .0.098 .3398.206 .2111 1110 1101 636 .0.0042 .2251.35 10011 10001 637 .0.098 .3398.206 .2111 1110 1101 636 .0.0042 .2251.35 10011 10001 637 .0.098 .3398.206 .2111 1110 1101 636 .0.0042 .2251.35 10011 10001 637 .0.098 .3398.206 .2111 1110 1101 636 .0.0042 .2251.35 10011 10001 637 .0.098 .3398.206 .2111 1110 1101 636 .0.0042 .2251.35 10011 10001 637 .0.098 .3398.206 .2111 1110 1101 636 .0.0042 .2251.35 10011 10001 637 .0.0001 638 .346.31 .3001 10001 636 .0.0042 .2251.35 10011 10001 636 .220 .0.0068 .3251.37 .70001 00001 628 .0.0001 638 .0.00001 636 .0.00000000000000000000000000000000										
2224.696 04411 04401 636 .0632 2614.235 20002 00001 628 .186 .2244.555 12211 12201 636 .0184 2641.26 20002 00001 628 .0184 2719.355 12212 12202 636 .129 2641.26 20002 00001 628 .022 2740.87 20011 20001 636 .0122 2765.00 20001 00001 627 .0018 .02240.87 20011 20001 636 .0122 2766.00 20001 00001 627 .0023 2242.066 20012 20002 636 .0258 2791.622 21101 01101 628 .0015 .2242.776 00021 00011 638 .00124	2229.724									
2279.55   12211   12201   636   .0384   2618.702   21102   01101   628   .0148   .022   .013   .0384   .024   .022   .018   .022   .018   .022   .018   .022   .022   .022   .020   .0201   .0221   .0221   .0221   .0221   .0221   .0221   .0221   .0221   .0221   .0221   .0221   .0221   .0221   .0221   .0221   .0221   .0221   .038   .00124   .0222   .0221   .0221   .038   .00124   .0221   .0221   .038   .0355   .0221   .0221   .0221   .038   .0555   .0354   .0221   .0221   .0221   .0221   .038   .0555   .0354   .0222   .0223   .0101   .026   .00024   .00224   .0222   .0224   .0222   .0224   .0222   .0224   .0										
2279.155   12212   12202   636   .129   .2641.26   .20002   .200001   .627   .018   .2022   .2240.887   .2011   .20001   .636   .0724   .2757.229   .20001   .00001   .628   .0023   .2242.766   .20012   .20002   .636   .0258   .2791.622   .21101   .0101   .628   .0015   .2242.776   .00221   .200021   .638   .00124   .2242.776   .00221   .200021   .638   .00124   .2242.776   .200021   .20001   .638   .00124   .2242.776   .200021   .20001   .638   .00124   .2245.177   .20211   .00011   .638   .0555   .1154.605   .22203   .0101   .626   .00074   .2245.17   .10011   .10001   .638   .0555   .1154.605   .22203   .0101   .626   .000074   .2248.156   .00112   .01001   .638   .0816   .0816   .3181.45   .21103   .00001   .626   .00067   .2248.361   .03111   .03301   .636   .0.280   .1275.113   .30003   .0101   .626   .00017   .2248.361   .03111   .03301   .636   .0.96   .3289.71   .21102   .00001   .626   .00017   .2250.60°   .11111   .1101   .636   .0.96   .3289.71   .21102   .00001   .626   .00017   .2250.74   .11112   .1102   .636   .1.91   .3119.340   .2102   .00001   .626   .00687   .2253.24   .0012   .00211   .00211   .00211   .0021   .637   .0.0364   .3340.471   .22002   .01101   .626   .00683   .2253.24   .0012   .00001   .636   .00042   .2253.24   .0012   .00001   .636   .00042   .00041   .2254.150   .01111   .0101   .638   .3.48   .3450.75   .33111   .03301   .636   .00413   .00041   .636   .00413   .2260.045   .0211   .02201   .636   .346   .3460.514   .21113   .1102   .636   .00413   .00041   .636   .00413   .00041   .636   .00413   .00041   .636   .00413   .00041   .636   .00413   .00041   .636   .00413   .00041   .636   .00413   .00041   .636   .00413   .00041   .636   .00413   .00041   .636   .00413   .00041   .636   .00413   .00041   .636   .00402   .00041   .0004   .636   .00402   .00041   .0004   .636   .00402   .00041   .0004   .636   .00402   .00041   .0004   .636   .00402   .00041   .0004   .636   .00402   .00041   .0004   .636   .00402   .00041   .0004   .636   .00402   .000402   .0004   .0004   .6										
2240.87 20011 20001 636 .0122 2776.00 20001 00001 627 .0023 2742.676 00021 00011 638 .00154 .	2239.355	12212	12202		.129					
2242.696 20012 20002 636 .0258										
2242.776         00021         00011         638         .00124           2242.73         02211         02201         638         .149         3125.323         30004         01101         626         .00024           2245.17         10011         10001         638         .0816         3181.4605         22203         01101         626         .00074           2248.356         01121         01101         636         .0280         3125.133         30003         01101         626         .00022           2250.607         11111         11102         636         1.52         3281.07         21102         00001         636         .00017           2250.677         11111         11102         636         1.91         3139.340         21102         00001         626         .0017           2251.01         02211         02201         637         0.0146         3196.529         30002         01101         626         .0417           2253.24         10012         10002         637         0.0088         3198.206         2111         1110         636         .0417           2260.045         02211         02201         636         34.6         3465.411										
2245.17         10011         10001         618         .0555         3154.605         22203         0101         626         .00074           2245.46         10012         10002         618         .0816         3181.45         21103         00001         626         .00687           2248.356         0121         01111         636         0.280         1275.113         30003         01101         626         .0102           2250.60°         11111         1110         b36         0.96         3281.07         21102         00001         628         .00017           2250.60°         11111         1110         636         1.91         3139.340         21102         00001         626         .00417           2251.71         0.2211         02201         637         0.0264         3140.471         22202         01101         626         .0063           2253.24         1.0011         10001         637         0.0098         3198.206         2111         1110         626         .0063           2253.24         1.0011         636         3.48         3450.75         13311         0330         636         .0113           2260.045         02211 <t< td=""><td></td><td>00021</td><td>00011</td><td>63B</td><td>.00124</td><td></td><td></td><td></td><td></td><td></td></t<>		00021	00011	63B	.00124					
2245, 36         10012         10002         638         0816         3181, 45         21103         00001         626         .00687           2248, 366         01121         01111         616         .0280         3275, 113         30003         01101         626         .0002           2248, 361         03311         03301         636         1,52         3281, 07         21102         00001         628         .00017           2250, 774         11112         11102         636         1,91         3381, 032         21102         00001         636         .00042           2251, 01         02211         02201         637         0.0264         3140, 471         22202         01101         626         .0063           2253, 53         10011         10002         637         0.0464         3196, 529         30002         01101         626         .0063           2253, 53         10011         10001         637         0.098         3198, 206         21111         1110         626         .00413           2260, 045         02211         02201         636         34.6         3460, 514         2111         1110         636         .0174           2261,										
2248. 356         01121         0111         636         .0280         3275.113         30003         01101         626         .0102           2248. 361         03311         03301         636         1.522         3281.07         21102         00001         628         .00017           2250. 60°         11111         11102         636         1.91         3339.340         21102         00001         626         .0417           2251. 01         02211         02201         637         0.0146         3349.471         22102         00101         626         .0063           2253. 53         10011         10002         637         0.0146         3396.529         30002         01101         626         .0063           2253. 53         10011         10001         638         3.48         3450.75         13311         03301         636         .0174           2260. 045         02211         02201         636         34.6         3460.514         21113         1110         636         .0474           2261. 920         10012         10002         636         20.3         3473.716         12212         02201         636         .1786           2260. 66										
2250.60°         11111         11101         636         0.96         3289.71         21102         00001         636         .0042           2250.7'4         11112         11102         636         1.91         3139.340         21102         00001         626         .0047           2251.01         0.2211         02001         637         0.0146         3139.340         21102         00101         626         .0063           2253.53         10011         10002         637         0.0146         3196.529         30002         01101         626         .00185           2254.15         10111         01101         638         3.48         3450.75         13311         03301         636         .0174           2260.045         02211         02201         636         34.6         3460.514         2111         11102         636         .0174           2261.920         10012         10002         636         20.3         3473.716         12212         02201         636         .3422           2262.66         01111         01101         637         0.628         3482.851         21112         11101         636         .450           2271.763 <t< td=""><td></td><td></td><td></td><td>636</td><td>.0280</td><td></td><td></td><td></td><td></td><td></td></t<>				636	.0280					
2250.7-4         11112         11102         636         1.91         3339.340         21102         00001         626         .0417           2251.01         02211         02201         637         0.0264         3349.471         22202         01101         626         .0063           2253.24         10012         10002         637         0.098         3398.206         2111         1110         626         .00185           2254.35         01111         01101         638         3.48         3450.75         13311         03301         636         .0174           2260.045         02211         02201         636         34.6         3460.514         21113         1110         636         .0174           2261.920         00021         00011         636         0.306         3465.431         2013         10001         626         .1786           2261.920         10012         10002         636         20.3         3473.718         12212         02201         636         .450           2262.66         01011         0101         636         12.3         3482.288         20013         10002         636         .450           2262.850         1001										
2251.01         02211         02201         637         0.0264         3349.471         22202         01101         626         .0063           2253.24         10012         10002         677         0.0146         3396.529         30002         01101         626         .00618           2253.53         10011         10001         637         .0098         3398.206         21111         11101         626         .00413           2250.045         02211         02201         636         34.6         3450.75         13311         03301         636         .0174           2260.045         02211         02201         636         34.6         3460.514         21113         11102         636         .0409           2260.045         02021         10012         10002         636         20.3         3473.716         12212         0201         636         .1786           2262.66         01101         0101         637         0.628         3482.281         2011         10001         636         .450           2262.80         10011         10001         636         12.3         3482.281         21112         11101         636         .450           227						3339.340	21102	00001		.0417 .14
2253.53         10011         10001         637         .0098         3398.206         21111         11101         626         .00413           2254.15         01111         01101         638         3.48         3450.75         13311         03301         636         .0174           2260.045         02210         02011         636         34.6         3450.75         142113         11102         636         .0409           2261.920         10012         10002         636         20.3         3473.716         12212         02201         636         .1786           2262.66         01111         01101         637         0.628         3482.238         20013         10001         636         .450           2262.65         10011         10001         616         12.3         3482.238         20013         10002         636         .450           2266.973         00011         10001         616         12.3         3482.881         21112         1110         636         .0134           2276.973         00011         00001         617         7.15         3498.780         10112         0101         636         .0134           2271.763         011	2251.01	02211	02201	637	0.0264		22202	01101	626	.0063 .14
2254.35         01111         0100         638         3.48         3450.75         13311         03101         636         .0174           2260.062         02211         02201         636         34.6         3460.514         21113         11102         636         .0409           2261.062         00021         00012         10002         636         20.3         3473.716         12212         02201         636         .3422           2262.66         01111         01101         637         0.628         3342.281         20013         10002         636         .450           2262.850         10011         10001         636         12.3         3482.851         21112         11101         636         .0134           2262.850         10011         10001         636         12.3         3482.851         21112         11101         636         .0134           2271.763         01111         01101         636         18.8         3490.390         10012         00001         638         .463           2271.763         01111         01101         636         0.088         3497.494         30001         01101         636         .0 pert           22										
2260.045         02211         02201         636         34.6         3460.514         21113         11102         636         .0409           2260.062         00021         00011         636         0.306         3465.433         2013         10001         626         .1786           2261.920         10012         10002         636         20.3         3471.716         12212         02201         636         .3422           2262.66         01111         01101         637         0.628         33482.218         20013         10002         636         .450           2265.973         00011         00001         636         12.3         3482.81         21112         1110         636         .0134           2271.763         01111         01101         636         818.         3490.399         10012         0001         638         .463           2271.367         06011         00001         617         7.15         3498.750         11112         0110         636         .0 pert           2774.367         06611         06601         626         0.0688         3500.590         21101         00001         636         .1052           2881.688 <t< td=""><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></t<>										
2261, 920         10012         10002         636         20,3         3473,716         12212         02201         636         .3422           2262,666         01111         01101         637         0.628         3482,813         2013         10002         636         .450           2262,850         10011         10001         636         12.3         3482,813         21112         11101         636         .0134           2271,763         00011         00001         628         38.8         3490,390         10012         00001         638         .463           2274,33         00011         00001         617         7.15         3497,540         3001         01101         636         .0 pert           2271,636         06611         06601         626         0.088         3500,590         21101         00001         626         .1052           2281,697         04411         04401         628         .0157         3504,933         14412         04401         626         .0372           2286,779         05411         02001         626         .0157         3504,933         14412         04401         626         .0372           2286,779	2260.045	02211	02201	636	34.6		21113	11102	636	.0409
262.66         01111         01101         617         0.628         3482.218         20013         10002         636         .450           2262.265         10011         10001         616         12.3         3482.818         20112         1110         636         .0134           2265.973         30011         00001         628         38.8         3490.390         10012         cocool         638         .463           2271.763         01111         01101         636         818         3497.494         30001         0110         636         .0 pert           2274.337         00011         00001         617         7.15         3498.750         11112         01101         636         .0 pert           2274.367         06611         06601         626         0.0068         3500.590         2110         00001         636         7.314           2282.69         04411         04401         628         .0157         3504.320         2100         11102         626         .0475           2281.490         00011         00001         636         9602.         3504.320         21101         11102         626         .0475           2286.797         <										
2202.850         10011         10001         636         12.3         3482.851         21112         11101         636         .0134           2265.973         00011         00001         628         38.8         3490.390         10012         c0001         638         .463           2271.763         01111         01101         636         818.         3497.464         30001         01101         636         .0 pert           2274.357         06011         06601         626         0.0068         3500.590         21101         00001         626         .1052           2281.688         22213         22203         626         .0369         3504.320         21101         00001         626         .0157           2281.699         04411         04401         628         .0157         3504.320         21001         1102         626         .0415           2281.490         00011         00001         636         9602.         3508.07         10012         00001         626         .0415           2286.797         05511         05501         628         0.0115         3509.207         21102         1101         628         .0642           2286.797										
2271.763 01111 01101 616 818.		10011	10001	636	12.3	3482.851	21112	11101	636	.0134
2774.33         09011         00001         617         7.15         3498.750         11112         0101         636         7.314           2274.367         06611         06601         626         0.0688         3500.590         21101         00001         626         .1052           2281.68R         22213         22203         626         .0389         3504.323         21101         11102         628         .0110           2282.69         04411         04401         628         .0157         3504.933         14412         04401         626         .0475           2284.90         00011         00001         636         9602.         3508.07         10012         00001         637         .0771           2286.779         05511         05501         626         .1942         3511.58         11112         01101         628         .00462           2286.779         05511         05501         626         .1942         3511.58         11112         01101         628         .161           2286.779         15212         12202         628         .0262         3517.323         20012         10001         628         .181           2286.779         <										
2774.367         06611         06601         626         0.0068         3500.590         21101         00001         626         .1052           2781.688         22213         22203         626         .0389         3504.320         21101         11102         628         .0110           2782.69         04411         04401         628         .0157         3504.320         21101         11102         628         .0110           2784.286         00011         00001         636         9602.         3508.07         10012         00001         637         .0771           2784.286         12211         12201         628         0.0115         3509.07         21100         1101         628         .00462           2786.779         05511         05501         626         .1942         3511.58         11112         01101         628         .181           2787.205         12212         12202         628         .0262         3517.323         20012         10001         636         .177           2288.152         13311         13101         1306         626         .1183         3525.205         10012         00001         626         .1034           <						3498.750	11112	01101		
2282.67 04411 04401 628 .0157 3504.933 14412 04401 626 .0475 2283.490 00011 00001 636 9602. 3508.07 10012 00001 637 .0771 2284.390 12211 12201 628 0.0115 3509.207 21102 11101 628 .00462 2286.779 05511 05501 626 .1942 3511.58 11112 01102 628 .181 2287.205 12212 12202 628 .0262 3517.323 20012 10001 636 .1277 2288.152 13311 13101 626 .1183 3525.205 10012 00001 628 .0588 2290.615 20012 20002 628 .0107 3527.703 30014 2003 626 .1034 2290.484 20011 20003 628 .0180 3527.740 10012 00001 636 94.2 2290.4715 13112 13102 626 .3125 3527.737 22212 12201 626 .0374 2293.420 21112 21102 626 .1946 3531.83 20013 10007 628 .181 2293.420 21112 21103 626 .1946 3531.83 20013 10007 628 .181 2293.621 21111 21101 626 .1946 3531.84 2011 1626 628 .181 2296.784 11111 11101 628 .325					0.0068					.1052 .14
2281.490         00011         00001         636         9602.         JS508.07         10012         00001         637         .0771           2286.779         05511         05501         628         0.0115         JS09.207         21102         1101         628         .00462           2286.779         05511         05501         626         .1942         J511.58         11112         01101         628         .181           2288.152         13311         1300         626         .1183         J525.505         10012         00001         636         .177           2290.615         20012         20002         628         .0107         J527.703         J0014         20003         626         .1034           2290.484         20011         20003         628         .0180         J527.703         J0014         20003         626         .1034           2290.715         13112         13102         626         .3125         J527.732         20012         20001         626         .1034           2290.715         13112         21102         626         .1919         J531.83         20013         10002         628         .181           2290.7627										
2284,286         12211         12201         628         0.0115         3509,207         21102         11101         628         .00462           2286,779         05511         05501         626         .1942         1511,58         11112         01101         628         .181           2287,205         12212         12202         628         .0062         1517,323         20012         10001         636         .177           2288,152         13311         13301         626         .1183         3525,205         10012         00001         828         .0588           2790,615         20012         20002         628         .0107         3527,703         30014         20003         626         .1034           2790,678         20012         20002         628         .0180         3527,703         30014         20003         626         .1034           2290,715         13112         13102         626         .3125         3527,757         22212         12201         626         .0374           2293,621         21112         21102         626         .1916         3511,83         20013         10067         628         .181           2293,621					9602.	3508.07	10012	00001	637	
2281.205         12212         12202         628         .0262         3517.323         20012         10001         636         .177           2288.152         13311         13101         626         .1183         3552.705         10012         00001         828         .0588           2790.615         20012         20002         628         .0107         3527.703         30014         20003         626         .1034           2290.484         20011         20003         628         .0180         3527.740         10012         00001         636         94.2           2290.715         13112         13102         626         .3125         3527.757         22212         12201         626         .0374           2293.420         21112         21102         626         .1919         3531.83         20013         10002         628         .181           2296.781         21111         21101         626         .1965         3533.492         11122         01101         626         .0353           2296.784         11311         11101         628         .325         3538.422         11112         01101         628         4.4489	2284.286	12211	12201	628	0.0115					.00462
2288.152         13311         13301         626         .1183         3525.205         10012         00001         828         .0588           2790.615         20012         20002         628         .0107         3527.703         30014         20003         626         .1014           2790.684         20011         20003         628         .0180         3527.740         10012         00001         636         94.2           2290.715         13112         13102         626         .3125         3527.757         22212         12201         626         .0374           2293.420         21112         21102         626         .1919         3511.83         20013         10067         628         .181           2293.621         21113         21101         626         .1965         3533.492         11112         01101         626         .0353           2296.784         11311         11101         628         .325         3536.822         11112         01101         628         4.449										
2270,615         20012         20002         628         .0107         1527,703         30014         2003         626         .1014           2270,484         20011         20003         628         .0180         3527,740         10012         00001         636         94.2           2270,715         13312         13302         626         .3325         3527,737         22212         12201         626         .0374           2279,621         21112         21102         626         .1919         3531,83         20013         10007         628         .181           2279,6714         11311         11101         628         .325         3538,482         11112         01101         628         4.449	2284.152				.1183	3525.205	10012	00001	828	.0588
2290.715     13112     13102     626     .3125     3527.757     22212     12201     626     .0374       2293.420     21112     21102     626     .1910     3531.83     20013     10067     628     .181       2293.621     21113     21103     626     .1965     3533.442     11122     01111     626     .0353       2296.784     11111     11101     628     .325     3536.822     11112     01101     628     4.449	2290.515	20012	20002	628	.0107					
2279, 420     21112     21102     626     .1919     3531.83     20013     10002     628     .181       229, 621     21113     21101     626     .1965     3533.942     11112     01101     626     .0353       2296, 784     11111     11101     628     .325     3538.822     11112     01101     628     4.449										
229,621     2111     21101     626     .3965     3533,942     1112     0111     626     .0353       2796,784     1111     1110     628     .325     3538,822     1112     01101     628     4,449					. 1917	3531.83	20013	10062	628	.161
	229 ) . 621	21113	21101	626	. 1965					
	2295.784 2295.022	11111 0331%	11101 03301	62A 62B	.325 .406	3538.822	20012	10001	628 628	4.449
2299,219 04411 04401 626 4.895 3542.601 21113 11102 626 3.147										

Table 10. Band Origins and Intensities for  ${\rm CO_2}$  (Contd)

 									<del></del>	
									.0	
Rand Center	Upper Level	Lower Level	Iso- tope	SV at 296K (multiply by	Band Center	Upper Level	Lower Level	Iso- tope	sv at 296K (multiply by	
v <sub>o</sub>	2000	Deve.	201-0		Vo.	Deve.	Dever	cope		
				10 <sup>-22</sup> mol <sup>-1</sup>					10 <sup>-22</sup> mol <sup>-1</sup>	
(cm <sup>-1</sup> )				cm <sup>2</sup> cm <sup>-1</sup> ) 5	(c=-1)				cap <sup>2</sup> cas <sup>-1</sup> ) 5	
 				C C , -					<del></del>	
3549.625	20013	10002	627	0.0224	4807.692	21113	01101	626	6.695	
3550.700	30012	20001	626	0.0195	4808.188	40002	01101	626	0. pert	
3552.841	12212	02201	626	31.25	4814.570	20012	00001	638	.0134	
3555.895 3556.749	21112 30013	11101	626	1.101	4821.500	20013 30013	00001 10001	627 626	.0744 .1376	
3558.595	11112	20002 01101	626 - 627	0.0629 .668	4839.737 4853.620	20013	00001	626	80.7	
3563.070	20012	10001	627	.0135	4871.46	21112	01101	636	.238	
3566.063	10022	00011	626	.208	4887.390	20012	00001	636	2.976	
3568.208 3571.143	20013 10012	10002 00001	626 628	33.78 52.2	4887.970 4896.185	12212 21112	00001 01101	626 628	(8.1-08 <sub>4</sub> ) .0893	
357R.670	22213	12202	626	0.138	4904.850	20012	00001	628	1.116	
3580.334	11112	01101	626	803.5	4925.010	20011	00001	638	0.00446	
3587.540	10011	00001	638	0.703	4928.910	21112	01101	627	.00744	
3590.86 3609.05	10012	00001	627 637	8.41 0.126	4931.083 4939.350	3113 20012	11102 00001	626 627	.0967 .2396	
3612.844	10012	00001	626	10350.	4942.512	30013	10002	626	1.414	
3621.283	20011	10001	636	0.283	4946.807	31112	11101	626	0.0595	
3621.570	20012	10002	636	0.435	4953.363	22212	02201	626	1.042	
3623.454 3625.176	21112 21111	11102 11101	636 636	.0433 .0324	4965.381	30012 21112	10001 01101	626 626	0.837 26.56	
3632.917	10011	00001	636	160.	4977.830	20012	00001	626	349.7	
3638.067	10011	00001	828	0.0392	4991.35	20001	00001	636	2.12	
3641.717	13311	03301	636	.0240	5013.785	21101	01101	636	0.1711	
3659.277	02211 20012	00001	626	(1.7-06 △)	5028.78	22211	02201	636	.00298 .227	
3655.42 3656.805	21112	10002 11102	628 628	.187 .0149	5042.57 5061.776	12211	00001	628 626	(9.2-08 △)	
3667.475	20012	10002	627	.0333	5062.442	30012	10002	626	.238	
3667.544	10021	00011	626	. 383	5064.680	21111	01101	628	.260	
3675.130 3675.694	10011 11121	00001 01111	628 626	47.8 0.0331	5068.910 5099.66	20011 20011	00001 00001	627 626	.0632 112.3	
3676.725	20011	10001	628	.164	5114.894	30011	10001	626	0.309	
3676.741	30012	20002	626	.0915	5123.20	21111	01101	626	10.64	
3679.644	30013	20003	626	.0986	5139.401	22211	02201	626	0.409	
3683.762	11111	01101	628	3.884						
3687.702 3687.40	21111 12211	01111 02201	628 628	0.0134 .143	5168.60 5217.669	01121 30001	00001 10002	636 <b>626</b>	.00372	
3692.41R	20012	10002	626	12.4	5247.030	10022	01101	626	.0101	
3603.640	10011	00001	627	10.2	5277.07	01121	00001	628	.00149	
3699.064	20011	10001	627	0.0279	5291.16	02221	01101	626	.0275	
3700.290 3702.345	21112 11111	11102 01101	626 627	3.549 0.771	5315.73 5349.36	01121 10021	00001 01101	626 626	.398 .00506	
3703.486	22212	12202	626	.1503	3349.30	10021	01101	020	.00306	
3705.927	30011	20001	626	.0551	5584.391	00031	10001	626	.00707	
3711.473	20011	10001	626	35.01	5687.166	00031	10002	626	.00751	
3713.714 3713.795	21111 22211	11101 12201	626 626	2.816 0.1094	5858.022	10022	00001	628	.00372	
3714.781	10011	00001	626	15000.	5951.600	30014	00001	636	.00179	
3723.249	11111	01101	626	1135.	5959.954	10021	00001	628	.00335	
3725.530	20011	10002	636	0.0078	5972.52	32214	02201	626	.00253	
3726.351 3726.647	14411 12211	04401 02201	626 626	.0499 48.5	5993.581 6020.795	30014 31114	00001	628 626	.00357 .0465	
3727.380	13311	03301	626	2.09	6072.343	40014	10001	626	.00104	
3783.14	20011	10002	628	0.0035	6075.983	30014	00001	626	.454	
3799.574 3814.248	30012 20011	20003 10002	626 626	.0028 0.770	6088.21 6100.30	31113	01101 01101	636 628	.00238	
3831.968	30011	20002	626	.00092	6119.618	30013	00001	636	.0290	
3858.109	21111	11102	626	.0251	6127.782 6149.760	30013	00001	628 626	.0238 .00179	
3856.657	30003	00001	628	.016	6170.090	41114 32213	11102 02201	626	.01265	
3987.610	30002	00001	628	.0149	6175.118	40014	10002	626	.02269	
4005.948	00021	01101	626	.00818 .14	6175.950	30013	00001	627	.00320	
4416.150	31104	00001	626	.00037 .15	6179.01 6196.174	41102 31113	00001 01101	626 626	(1.5-06 π) .268	
4508.749 4529.870	00021 40004	00001 01101	638 626	.00186	6205.503	40013	10001	626	.0127	
4578.090	32203	01101	626	.00018 .20	6227.924	30013	00001	626	4.27	
4591.118	31103	00001	626	.00205 .18	6241.964	30012	00001	636	.0461 .00409	
4614.779	01121	01101	628	.01042	6243.57 6254.592	31112 30012	01101	636 628	.01414	
4639.502 4655.205	00021 00021	00001	628 627	.1302 .0127	6265.170	31112	01101	628	.00119	
4671.680	22213	02201	636	.00149	6298.110	30012	00001	627	.00275	
4685.780	30014	10002	636	.00186	6308.278	40013	10002	626	.02455	
4687.796	30014	10001	626	.00521	6318.17	41113 40012	11102 10001	626 676	.00179 .0119	
4692.180	20013 21113	00001 01101	638 636	.00260	6347.854	30012	00001	626	4.27	
4708.52 4733.50	23313	03301	626	.00670	6356.293	31112	01101	626	0.327	
4743.70	21113	01101	628	.0335	6359.287	32212	02201	626	.0116	
4748.058	20013	00001	636	.214	6363.616	30011	00001	636	.0127	
4753.450 4755.705	31102 31114	00001 11102	626 626	.00298 .10 .0179	6388.015 6397.545	41101 31111	00001 01101	626 636	(4.8-06 T) .00119	
4768.541	22213	02201	626	.2604	6429.172	30011	00001	628	.00112	
4784.675	20023	00011	626	.00149	6466.440	20023	01101	626	.00104	
4786.688	31113	11101	626	.0119	6498.67 6503.081	12222 30011	01101 00001	626 626	.00119	
4790.571 4791.260	30014 20013	10002 00001	626 628	.1562 .469	6532.653	40011	10001	626	.00130	
					1				***	

Table 10. Band Origins and Intensities for  ${\rm CO}_2$  (Contd)

Band Center	Upper. Level	Lover	Iso-	SV at 296K	
	Devel	Level	tope	(multiply by	
v <sub>o</sub>				10 <sup>-22</sup> mo1 <sup>-1</sup>	
(cm <sup>-1</sup> )		_		cm <sup>2</sup> cm <sup>-1</sup> ) <sup>3</sup>	,
6536.445	31111	01101	626	.0476	
6537.958	11122	00001	626	.0223	
6562.444	32211	02201	626	.00223	
6679.709	11121	00001	626	.0283	
6745.115	01131	01101	636	.01339	Notes to Table IV-2.2
6780.215	00031	00001	636	.1637	'
6860.410	03331	03301	626	.00201	Bands deriving all their intensity from J-dependent
6867.280	11131	11101	626	.00112	perturbation are designated o pert, when one near
6870.796	11132	11102	626	.00241	band provides the intensity, TT, when the listed
6885.150	01131	01101	628	.00402	intensity is multiplied by $m(m+1)$ , and $\Delta$ , when the
6897.751	02231	02201	626	.0424	listed intensity is multiplied by m <sup>2</sup> (m+1) <sup>2</sup> .
6905.770	10031	10001	626	.0171	0. 4-44-4-4-4-4-4-4-4-4-4-4-4-4-4-4-4-4-4
6907.144	10032	10002	626	.0290	Q designates bands with intensity below the criterion limit, whose Q - branches are
6922.210	00031	00001	628	.0521	significant.
6935.150	01131	01101	626	1.131	**************************************
6945.610	00031	00001	627	0.0112	
6972.578	00031	00001	626	14.95	
7283.981	40015	00001	626	0.00186	•
7460.530	40014	00001	626	.0428	
7401.51	40013	00001	636	.00112	
7583.265	41113	01101	626	.00833	
7593.690	40013	00001	626	.1064	
7616.620	51102	00001	626	(1.12-06 Tr)	
7734.452 7757.621	40012 41112	00001	626	.0279	
7901.479	21122	01101	626	.00298	114
7920.840	40001	00001	626 626	.00149 .0	018
7981.180	10032	00001	636	.00232	
8084.060	12232	02201	626	.00232	
8089.84	10031	00001	636	.00707	
8103.578	20033	10002	626	.00205	
8120.104	10032	00001	628	.00203	
8128.783	20032	10001	626	.00071	
8135.886	11132	01101	626	.0402	
8192.556	10032	00001	626	.424	
8220.363	10031	00001	628	.00201	
8243.163	20031	10001	626	.00108	
8254.800	12231	02201	626	.00164	•
8276.767	11131	01101	626	.0461	
8293.957	10031	00001	626	.614	
9388.990	20033	00001	626	.00415	
9478.051	21132	01101	626	.00180	•
9516.970	20032	00001	626	.0233	
9631.350	20031	00001	626	0093	

of  $\zeta^{V}$  included in Table 9. Note that when  $\zeta_{V}$  is larger than 0.01, the total band strength, if defined as the sum of the Q, R- and P-branch lines,  $\frac{r}{m}S_{m}$ , may be much larger than  $S_{V}^{0}$ , its value when  $\zeta_{V} = 0$ . The entry in Table 10 is  $S_{V}^{0}$ , not  $\frac{r}{m}S_{m}$ .

As a higher-order effect of Coriolis interactions, transitions with  $\ell$ ' -  $\ell$ " =  $\pm$ 2 also become allowed, the effect increasing as m<sup>2</sup>, so that a few such bands are intense enough to appear; here we list the value of  $S_{V}^{O}$  in the formula  $S_{m} = S_{V}^{O} (|m| + m^{2}) \exp{[(-1.439E'')/T]/Q_{T}}$ .

There are also a few special cases of near-or crossing-perturbations, where a normally very weak band "borrows" intensity from a stronger neighbor. A notable example is represented by the bands at 4808.186 cm<sup>-1</sup>, where the 40002-01101 band with zero intensity, resonates with the 21113-01101 band at 4807.692 cm<sup>-1</sup>. The positions and intensities of the individual lines are here calculated using an appropriate Coriolis constant and dividing the strength of 21113-01101 according to the degree of perturbational mixing.

# 4.2.3 CO<sub>2</sub> LINE HALF-WIDTHS

The half-widths for  $CO_2$  were assigned by a linear function of the rotational quantum number. The work of Yamamoto, Tanaka and Aoki (1969) gave methods of estimating half-widths for the 15  $\mu$ m and 4.3  $\mu$ m regions, but the differences between their limited comparisons of calculated values and laboratory measurements did not seem to warrant any more complicated procedure in arriving at a half-width dependence upon J for  $CO_2$ .

### 4.3 Ozone

The band centers and intensities of all bands included in the compilation are given in Table 11.

The pure rotational transitions of ozone have been calculated using the molecular constants of Lichtenstein, Gallagher, and Clough (1971) obtained from microwave measurements. Transitions with upper state J less than 61 and intensities greater than  $3.5 \times 10^{-24} \, \mathrm{cm}^{-1}/\mathrm{mol\text{-}cm}^2$  have been tabulated using a value of  $\mu$ = 0.53D for the dipole moment. Lines with  $K_a$  less than 10 should be accurate to 0.001 cm<sup>-1</sup>. Multiplets up to  $K_a$  = 12 ( $\approx$ 100 cm<sup>-1</sup>) have been observed and the calculated contours agree within the experimental accuracy (see Gebbie et al, 1966). At higher values of  $K_a$ , the calculations become increasingly less certain. However, even the highest value of  $K_a$  included in the listing (that is,  $K_a$  = 20) is substantially less than the value of K for which the calculation is divergent. The mean line width has been determined to be 0.11 (Lichtenstein et al, 1971).

Band Center	$\Sigma_{ m i}$ S $_{ m i}$	Vibrational	Isotope	
cm <sup>-1</sup>	$\frac{\operatorname{cin}^{-1}}{\operatorname{mol/cm}^{2}}$	Upper State	Lower State	
0. 700.930 1007.693 1007.996 1021.096 1027.096 1028.096 1042.096 1103.157 2110.790 2785.241	4.13 x 10 <sup>-19</sup> 6.70 x 10 <sup>-19</sup> 9.49 x 10 <sup>-21</sup> 2.49 x 10 <sup>-20</sup> 4.23 x 10 <sup>-19</sup> 1.62 x 10 <sup>-19</sup> 5.16 x 10 <sup>-20</sup> 1.29 x 10 <sup>-17</sup> 3.47 x 10 <sup>-19</sup> 1.33 x 10 <sup>-18</sup> 2.32 x 10 <sup>-20</sup> 1.10 x 10 <sup>-19</sup>	000 010 101 001 011 002 001 001 100 101	000 000 100 000 010 001 000 000 000	666 666 686 686 666 668 666 666

Table 11. Ozone Transitions Included in Data Compilation

For the  $\nu_2$  fundamental of ozone, upper-state molecular constants have been obtained from microwave data by Tanaka and Morino (1970a). For a discussion of the determination of the band center see Tanaka and Morino (1970b). Transitions up to J = 60 with intensities greater than 3.5 x  $10^{-23}$  cm<sup>-1</sup>/mol-cm<sup>2</sup> have been tabulated. The dipole moment constant for the  $\nu_2$  fundamental has been taken as  $(\partial \mu/\partial q_2) q_2 = 0.048D$  giving a band intensity of 6.76  $10^{-19}$  cm<sup>-1</sup>/mol-cm<sup>2</sup> based on the measurements of McCaa and Shaw (1968).

The  $\nu_3$  and  $\nu_1$  regions of the ozone spectrum have been studied by Clough and Kneizys (1965, 1966), and Tanaka and Morino (1968). The positions of the  $\nu_1$  and  $\nu_3$  transitions for the main isotope are expected to be accurate to 0.01 cm<sup>-1</sup> for J less than 40 and  $K_a$  less than eight with a degradation of accuracy for higher values of the quantum numbers. In conformity with the results of McCaa and Shaw (1968), the band intensity of  $\nu_3$  has been taken as  $130 \times 10^{-19} \, \mathrm{cm}^{-1}/\mathrm{mol\text{-cm}^2}$ .

Also, more lines have been included than were given in the report of Clough and Kneizys (1965). Goldman, et al (1970) have found that the absorption by large ozone amounts could not be satisfactorily explained without introducing the hot bands and the isotopic bands. Since the energy levels are known for the 101, the 100 and the 010 vibrational levels, transitions for the  $101 \leftarrow 100$  and  $101 \leftarrow 001$  bands may be calculated directly. The line positions for these bands with J less than 30 and  $K_a$  less than six are presumed accurate to  $\pm 0.03$  cm<sup>-1</sup>. The line positions for the  $011 \leftarrow 010$  hot band have been obtained by applying a calculated shift of -21.0 cm<sup>-1</sup> to the  $\nu_3$  transitions of the main isotope. For J less than 30 and  $K_a$  less than six an error of up to 1 cm<sup>-1</sup> may be expected. For the  $002 \leftarrow 001$ 

hot band, a calculated shift of -15.0 cm  $^{-1}$  has been applied to the  $\boldsymbol{\nu}_3$  transitions of the main isotope. In this case, the rotational levels of the upper- and lower-vibrational states are not accurately described, and these lines must be considered to be useful only for their general contribution to the low-resolution absorption in the region. These shifts have been calculated using harmonic frequencies and anharmonic corrections determined from an analysis of the available vibrational data.

For the 668 and 686 isotopes, shifts of  $-13.1~{\rm cm}^{-1}$  and  $-34.1~{\rm cm}^{-1}$  respectively have been determined from force constant calculations using the structural constants given by Tanaka and Morino (1968). These shifts have similarly been applied to the original  $\nu_3$  line calculations, neglecting the isotopic effect on the rotational constants. Consequently, only the general contribution to low-resolution spectra by these lines is valid. The intensities of the hot bands and the isotopic bands have been determined by applying the appropriate Boltzmann correction, isotopic abundance factor, dipole moment matrix element value, and degeneracy factor to the intensities of the  $\nu_3$  fundamental.

Although the addition of the isotopic bands and the hot bands gives improved agreement between calculated absorption and the observed absorption for large ozone amounts, it appears that an intensity anomaly still exists. In the P branch region ( $\sim 1000~\rm cm^{-1}$ ) the calculated intensity is evidently too low, while in the R branch region the calculated intensity is too high. Until better intensity measurements are available, it will be difficult to obtain experimental F factors (see Section 3.2).

The  $(\nu_1 + \nu_3)$  combination band (101  $\leftarrow$  000) has been observed and analyzed using the rigid rotor approximation by Trajmar and McCaa (1964). The value of the band center was found to be 2110.79 cm<sup>-1</sup>. The resolution and calibration accuracy of the observed spectra were not good, so that the line positions up to J = 20 and  $K_a = 4$  are accurate to only 0.3 cm<sup>-1</sup>. The error in line position is expected to be significantly greater for higher quantum numbers. The band intensity for the tabulated lines is 1.19 x  $10^{-18}$  cm<sup>-1</sup>.

The ( $\nu_1 + \nu_2 + \nu_3$ ) combination band (111  $\leftarrow$  000) at 2785.241 has been studied by Snider and Shaw (1971). The rigid rotor analysis used gives line positions for J less than 25 and K<sub>a</sub> less than 6 accurate to 0.1 cm<sup>-1</sup>. The intensity for this band is 2.46 x 10  $\frac{\text{cm}^{-1}}{\text{mol/cm}^2}$  and was also obtained from McCaa and Shaw (1968).

Constants for the 3  $\nu$  3 band (003  $\leftarrow$  000) have been obtained from a second order calculation using the results of Tanaka and Morino (1968). The band intensity has been taken as  $1.12 \times 10^{-19}$  cm<sup>-1</sup>/molecule-cm<sup>-2</sup> from McCaa and Shaw (1968). The accuracy of the line positions should not be in error by more than + 5 cm<sup>-1</sup>.

#### 4.4 Nitrous Oxide

Nitrous oxide is an asymmetric linear molecule (N-N-O) with three fundamental vibration-rotation bands,  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$ , at 1284.907, 588.767, and 2223.756 cm<sup>-1</sup>, respectively, for the main isotope. As for CO<sub>2</sub>,  $\nu_1 \cong 2$   $\nu_2$  so that Fermi resonance occurs between these two levels, causing shifts of the band centers from the positions otherwise expected. Five different isotopes provide significant absorption. When no reference to a particular isotope is made, the most abundant one, 446, is implied. The abbreviated notations and natural abundances of each isotope used to calculate intensities of the isotopic bands are (446), 99.043 percent; (456), 0.358 percent; (546), 0.358 percent; (448), 0.199 percent; and (447), 0.040 percent. These values differ slightly from those given in Table 4, the difference arising from slight differences in the oxygen and nitrogen natural abundances taken from the 48th edition and the 42nd edition of the Handbook of Physics and Chemistry.\* The 48th edition values were used in the construction of Table 4. These abundance differences are very small, but can be accounted for by modifying the line intensities accordingly.

#### 4.4.1 LINE POSITIONS

Table 12 lists the constants used to calculate the line positions. Values of the vibrational energy, G, are relative to the  $00^{\circ}0$  level for each isotope and are probably accurate to a few thousandths of a cm<sup>-1</sup> for the 446 isotope. The uncertainty is much greater for some of the levels of the rarer isotopes. The majority of the constants for the 446 isotope and a few for the other isotopes are from Pliva (1964, 1968a, 1968b). Most of the other values have been derived by Benedict (private communications) from a variety of data.

Line positions for the P- and R-branches can be calculated by inserting the constants from Table 12 into Eq. (6). The selection rules are:  $\Delta J = 0, \pm 1$ ;  $\Delta \ell = 0, \pm 1$ ; and  $J = 0 \leftrightarrow J = 0$ . The allowed values of J for a given vibrational level must be taken into account in order to determine missing lines. For example, in a  $\phi \leftarrow \Delta$  band ( $\ell' = 3 \leftarrow \ell'' = 2$ ) the following lines are missing because of rotational energy levels that are not allowed: P1, P2, P3, Q0, Q1, Q2, R0 and R1.

A few lines of the  $10^{0}1$ ,  $06^{0}0$ ,  $06^{2}0$ , and  $10^{0}1 - 10^{0}0$  bands are shifted from the positions based on the constants in Table 12 because of Fermi interactions. These are discussed in more detail below and summarized in Table 15.

<sup>\*</sup>Published by the Chemical Rubber Co., Cleveland, Ohio

Table 12. Vibrational Energy Levels and Molecular Constants for  ${\rm N_2O}$ 

F	Τ = =			T
Energy Level	G	В	D Multiply	H Multiply
			by 10 <sup>-7</sup>	by 10 <sup>-12</sup>
	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )
		Isotope 446		
00 <sup>0</sup> 0	0	0.4190113	1.795	1.17
01 <sup>1°</sup> 0	588.767	0.4191777	1.785	1.17
01 <sup>1d</sup> 0	588.767	0.4199695	1.785	1.17
02 <sup>0</sup> 0	1168.134	0.4199193	2.445	1.17
02 <sup>2C</sup> 0	1177.750	0.4201253	1.165	1.17
02 <sup>2d</sup> 0	1177.750	0.4201253	1.795	1.17
10 <sup>0</sup> 0	1284.907	0.4172563	1.775	1.17
03 <sup>1°</sup> 0	1749.058	0.4196063	2.195	1.17
03 <sup>1d</sup> 0	1749.058	0.4210883	2.195	1.17
03 <sup>3d</sup> 0	1766.958	0.420674	1.805	2.20
03 <sup>3c</sup> 0	1766.958	0.420674	1.805	0.14
11 <sup>10</sup> 0	1880.268	0.4174673	1.765	1.17
11 <sup>1d</sup> 0	1880,268	0.4183803	1,775	1.17
04 <sup>0</sup> 0	2322,570	0.4206113	4.095	16.17
04 <sup>2°</sup> 0	(2331.15)	0.4210113	1,350	1.17
$04^{2d}0$	(2331.15)	0.4210113	2.50	1.17
12 <sup>0</sup> 0	2461.998	0.4181483	2.465	3.77
12 <sup>20</sup> 0	2474.785	0.4187143	1,210	1.17
12 <sup>2d</sup> 0	2474.785	0.4187143	1,700	1.17
20 <sup>0</sup> 0	2563.341	0.4224193	1.645	1.17
00 <sup>0</sup> 1	2223.756	0.4155613	1.795	1.17
05 <sup>1°</sup> 0	2897.876		2.085	1.17
05 <sup>1d</sup> 0	2897.876		2.355	1.17
13 <sup>1c</sup> 0	3046.213	0.4177633	2.145	1.17
13 <sup>1d</sup> 0	3046.213	0.4193783	2,165	1.17
13 <sup>30</sup> 0	3067.749	0.419109	1.805	0.47
13 <sup>3d</sup> 0	3067.749	0.419109	1,805	1.87
t control of the cont	•	•	•	•

Table 12. Vibrational Energy Levels and Molecular Constants for  ${\rm N_2O}$  (Contd)

		5	T.	1.1
Energy Level	G	В	D Multiply	H Multiply
			by $10^{-7}$	by 10 <sup>-12</sup>
	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )
		Isotope 446 (Contd)		
10			:	
21 <sup>1c</sup> 0	3165.857	0.4158333	1.595	1.17
21 <sup>1d</sup> 0	3165.857	0.4169163	1.595	1.17
01 <sup>1c</sup> 1	2798.290	0.4157723	1.795	1.17
01 <sup>1d</sup> 1	2798.290	0.4165473	1.795	1.17
, 14 <sup>0</sup> 0	3620.941	0.4187873	3.885	14.17
14 <sup>2°</sup> 0	3631.601	0.4190143	0.375	1.17
14 <sup>2d</sup> 0	3631.601	0.4190143	2.045	1.17
22 <sup>0</sup> 0	3748.252	0.4163273	2.395	2.77
22 <sup>2</sup> c0	3766.060	0.4172013	1.200	1.17
22 <sup>2d</sup> 0	3766.060	0.4172013	1.560	1.17
30 <sup>0</sup> 0	3836.373	0.4141473	1,385	1.17
02 <sup>0</sup> 1	3363.974	0.4165443	2.445	1.17
02 <sup>2°</sup> 1	3373.137	0.4167523	1.195	1.17
02 <sup>2d</sup> 1	3373.137	0.4167523	1.795	1.17
10 <sup>0</sup> 1	3480.821	0.4137843	1.745	1.17
23 <sup>1c</sup> 0	4335.798	0.4159193	2.045	1.17
23 <sup>1d</sup> 0	4335.798	0.4176813	2.115	1.17
31 <sup>1c</sup> 0	4446.379	0.4143703	1.625	1.17
31 <sup>1d</sup> 0	4446.379	0.4156713	1.365	1.17
03 <sup>1°</sup> 1	3931.258	0.4162253	1.915	1.17
03 <sup>1d</sup> 1	3931.258	0.4176843	1.925	1.17
03 <sup>3c</sup> 1	3948.344	0.417327	1.815	0.14
03 <sup>3d</sup> 1	3948.344	0.417327	1.815	2.20
11 <sup>1c</sup> 1	4061.979	0.4140513	1.775	1.17
11 <sup>1d</sup> 1	4061.979	0.4149343	1.735	1.17
40 <sup>0</sup> 0	5105.65	0.4131913	1.795	1.17
32 <sup>0</sup> 0	5026.34	0.4143113	1.795	1.17
20 <sup>0</sup> 1	4730.828	0.4121163	1.625	1.17
12 <sup>0</sup> 1	4630.164	0.4147633	2.475	4.17
12 <sup>2c</sup> 1	4642.463	0.4151583	1.315	1.17
12 <sup>2d</sup> 1	4642.463	0.4151583	1.315	1.17
002	4417.379	0.4120963	1.765	1.17

Table 12. Vibrational Energy Levels and Molecular Constants for N<sub>2</sub>O (Contd)

Energy Level	(cm <sup>-1</sup> )	B (cm <sup>-1</sup> )	D Multiply by 10 <sup>-?</sup> (cm <sup>-1</sup> )	II Multiply by 10 <sup>-12</sup> (cm <sup>-1</sup> )					
	Isotope 446 (Contd)								
21 <sup>1c</sup> 1	5319.175	0.4124313	1.675	1.17					
21 <sup>1d</sup> i	5319.175	0.4134703	1.555	1.17					
01 <sup>1c</sup> 2	4977.695	0.4123583	1.785	1.17					
01 <sup>1d</sup> 2	4977.695	0.4131183	1.785	1.17					
	·	Isotope 456							
00 <sup>0</sup> 0	0	0.4189821	1.75						
01 <sup>1c</sup> 0	575.5	0.419095	1.75						
01 <sup>1d</sup> 0	575.5	0.419891	1.75						
10 <sup>0</sup> 0	1280.5	0.41719	1,72						
11 <sup>10</sup> 0	1861.9	0.41734	1.71						
11 <sup>1d</sup> 0	1861.5	0.41820	1.70						
20 <sup>0</sup> 0	2554.3	0.41545	1.67	·					
00 <sup>0</sup> 1	2177.659	0.41568	1.75	·					
01 <sup>1c</sup> 1	2739.63	0.415855	1.75						
01 <sup>1d</sup> 1	2739.63	0.416605	1.75						
10 <sup>0</sup> 1	3430.95	0.41387	1.72						
	<del></del>	Isotope 546							
00 <sup>0</sup> 0	C	0.4048564	1,64						
01 <sup>1c</sup> 0	585.320	0.4050304	1.65						
01 <sup>1d</sup> 0	585.320	0.4057724	1.65						
10 <sup>0</sup> 0	1269.894	0.403269	1.60						
11 <sup>10</sup> 0	1863.080	0.4034614	1.59						
11 <sup>1d</sup> 0	1863.080	0.4043814	1.57						
20 <sup>0</sup> 0	2534.21	0.401870	1.45						
00 <sup>0</sup> 1	2201.604	0.401495	1.65						
01 <sup>1c</sup> 1	2745,709	0.4017054	1.65						
01 <sup>1d</sup> 1	2745.709	0.4024104	1.65						
10 <sup>0</sup> 1	3443.659	0.399876	1.60						

Table 12. Vibrational Energy Levels and Molecular Constants for  ${\rm N_2O}$  (Contd)

Energy Level	G	В	D Multiply	H Multiply
	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )	by 10 <sup>-7</sup> (cm <sup>-1</sup> )	by 10 <sup>-12</sup> (cm <sup>-1</sup> )
		Isotope 448		
00°0	o	0.395577	1.65	
01 <sup>1°</sup> 0	584.1	0.395749	1.65	! !
01 <sup>1d</sup> 0	584.1	0.396461	1.65	
10 <sup>0</sup> 0	1247.9	0.394057	1.55	
11 <sup>10</sup> 0	1839.8	0.39430	1.56	
11 <sup>1d</sup> 0	1839.8	0.39513	1.50	
20 <sup>0</sup> 0	2491.3	0.39279	1.31	
00 <sup>0</sup> 1	2218.97	0.392317	1.65	
01 <sup>1°</sup> 1	2788.80	0.392549		·
01 <sup>1d</sup> 1	2788.80	0.393209		
10 <sup>0</sup> 1	3439.1	0.39078	1.55	
		Isotope 447		
00 <sup>0</sup> 0	0	0.406691	1.72	
01 <sup>1c</sup> 0	586.3	0.406860	1.72	
01 <sup>1d</sup> 0	586.3	0.407610	1.72	
10 <sup>0</sup> 0	1265.5	0.405961	1.67	
00 <sup>0</sup> 1	2221.3	0.40334		
01 <sup>1C</sup> 1	2793.55	0.40357		
01 <sup>1d</sup> 1	2793.55	0.40430		

#### 4.4.2 LINE INTENSITIES

Each band system contains a main band and associated hot bands that arise from transitions from excited energy levels with the same changes  $\Delta v_1$ ,  $\Delta v_2$ , and  $\Delta v_3$  in the vibrational quantum numbers as in the main band. The change  $\Delta t$  may be either 0 or  $\pm$  1 within the same band system. For example, the  $0^{\circ}$ 01 band is the main band in a system that also contains the hot bands  $01^{1}1 \pm 01^{1}0$ ,  $02^{\circ}1 \pm 02^{\circ}0$ ,  $02^{2}1 \pm 02^{2}0$ ,  $10^{\circ}1 \pm 10^{\circ}0$ , and many others from higher excited energy levels. The relative intensities of the hot bands decrease with increasing value of the lower energy level because of the decrease in its population. Thus, only a few of the hot bands are usually significant. Corresponding bands of the rare isotopic molecules are also part of the system. The main band of the common isotope accounts for 78 percent to 89 percent of the entire system for  $296^{\circ}$ K samples, depending on the band system.

Table 13 summarizes the normal band systems containing lines with intensities greater than 4 x 10<sup>-23</sup> molecules <sup>-1</sup> cm<sup>2</sup> cm<sup>-1</sup>. Each band system is identified by the main band whose center position is given. The intensities are based on recent measurements of the quantity f(-1/u) fn T d $\nu$  by Burch et al, (1971a, 1971b, 1971c, 1972). The integration was performed over the entire band system, and u is the N<sub>2</sub>O thickness in molecules cm<sup>-2</sup>. The intensity, S<sub>Q</sub>, of only the Q-branch of the band at 1974.571 cm<sup>-1</sup> is listed because the P and R branches contain no lines with intensities above the cut-off. The Q-branch may be significant although each of its lines is very weak because they occur very close together. Bands containing the 06<sup>0</sup>O and 06<sup>2</sup>O levels are not listed because the band systems are very weak. However, as a result of Fermi interaction between a few of the rotational levels, the intensities of the corresponding lines are anomalously high and their positions are shifted. These lines are discussed in more detail below.

Table 14 lists the intensities of each of the bands with lines above the cutoff intensity, nominally  $4 \times 10^{-23}$  molecules  $^{-1}$  cm $^{2}$  cm $^{-1}$ . Each line entry in the table corresponds to a given band, and blank lines occur before and after each band system. Note that 16 bands are listed for the  $00^{0}$ 1 band system, whereas only 1 or 2 bands are listed for some of the weaker systems.

Each rotational level within a vibrational level for which quantum number  $\ell \neq 0$  is split into two sublevels normally indicated by "c" and "d" (see section 3.1.1). A band involving two  $\Delta$  levels, or two  $\pi$  levels, or one of each level consists of two sub-bands, one from the c portion of the lower level and one from the d portion. The  $c \leftarrow c$  portion of the first sub-band contains only P- and R-branches, whereas the  $d \leftarrow c$  portion contains the Q-branch. Similarly, the  $d \leftarrow d$  and the  $c \leftarrow d$  portions of the second sub-band contain the P+R branches and the Q-branch, respectively. The intensities,  $S_{n,n}$ , given in Table 14 are the total for both sub-bands.

Table 13. Summary of  ${\rm N_2O}$  Band Systems

		2	
Center of Main Band (cm <sup>-1</sup> )	Upper Level	Lower Level	Intensity of System  Multiply by 10 <sup>-20</sup> Molecules <sup>-1</sup> cm <sup>2</sup> cm <sup>1</sup>
588.767	0110	00 <sup>0</sup> 0	118 <u>+</u> 9
696.140 938.849 1168.134 1284.907	10 <sup>0</sup> 0 00 <sup>0</sup> 1 02 <sup>0</sup> 0 10 <sup>0</sup> 0	01 <sup>1</sup> 0 10 <sup>0</sup> 0 00 <sup>0</sup> 0 00 <sup>0</sup> 0	$\begin{array}{r} 0.354 + 0.020 \\ 0.254 \mp 0.010 \\ 38.5 + 1.5 \\ 996 + 40 \end{array}$
1634.989 1749.058 .1880.268 1974.571 2223.756	00 <sup>0</sup> 1 03 <sup>1</sup> 0 11 <sup>1</sup> 0 20 <sup>0</sup> 0 00 <sup>0</sup> 1	01 <sup>1</sup> 0 00°0 00°0 01 <sup>1</sup> 0 00°0	$0.278 + 0.02$ $0.241 + 0.02$ $1.66 + 0.08$ $S_{Q} = 0.024 + 0.002$ $5710 + 250$
2322.624 2461.998 2563.341 2798.290 3363.974 3480.821 3620.941 3748.252 3836.373 4061.979 4335.798 4417.379 4630.164 4730.828 4977.695 5026.34 5105.65	04°0 12°0 20°0 0111 02°1 10°1 14°0 22°0 30°0 1111 2310 00°2 12°1 20°1 0112 32°0 40°0	00°0 00°0 00°0 00°0 00°0 00°0 00°0 00°	$\begin{array}{c} 2.7 + 0.3 \\ 33.4 + 1.5 \\ 135 + 7 \\ 9.62 + 0.96 \\ 10.6 + 0.5 \\ 197 + 10 \\ 0.56 + 0.02, -0.05 \\ 4.12 + 0.2 \\ 8.15 + 0.4 \\ 0.111 + 0.006 \\ 0.1 + 0.1, -0.07 \\ 6.9 + 0.7 \\ 0.68 + 0.07 \\ 4.4 + 0.4 \\ 0.070 + 0.008 \\ 0.29 + 0.04 \\ 0.29 + 0.03 \\ \end{array}$

Table 14. N<sub>2</sub>O Band Intensities

		*:		
Band Center	Upper	Lower	Isotope	S <sub>v</sub> at 296K
$ u_{\rm c}$	Level	Level		(Multiply by 10 <sup>-20</sup>
(cm <sup>-1</sup> )				Molecules cm <sup>2</sup> cm <sup>-1</sup> )
(em )				Molecules chi chi /
588.767	0110	00 <sup>0</sup> 0	446	98.4
579.367	02 <sup>0</sup> 0 02 <sup>2</sup> 0	01 <sup>1</sup> 0 01 <sup>1</sup> 0	446	4.90
588.983	0220	01 10	446	11.26
580.924	0310	02 <mark>0</mark> 0	446	0.599
571.308	0330	0220	446	0.256
589.208	03 <sup>3</sup> 0 11 <sup>1</sup> 0		446	0.958
595.361	1110	10°0	446	0.216
585.320	0110	00°0 00°0	546	0.356
575.5	0110	0000	456	0.356
586.3	01 <sup>1</sup> 0 01 <sup>1</sup> 0	0000	447	0.039
584.1	}		448	0.197
696.140	10 <sup>0</sup> 0	01 <sup>1</sup> 0	446	0.294
938.849	00 <sup>0</sup> 1	10 <sup>0</sup> 0	446	0.223
1168.134	0200	00 <mark>0</mark> 0 010	446	31.7
1160.291	0310	01 <sup>1</sup> 0	446	5.72
1154.436	04 <mark>0</mark> 0	l naon	446	0.201
1153.40	03 <sup>1</sup> 0 04 <sup>0</sup> 0 04 <sup>2</sup> 0	0220	446	0.228
1177.750	02 <sup>2</sup> 0	0000	446	See Note A
1284.907	1000	00 <sup>0</sup> 0 01 <sup>1</sup> 0	446	872.
1291.501	1110	0110	446	100.6
1293.864	12 <sup>0</sup> 0	0200	446	3.16
1297.035	1220 2000 1310 1330	0220	446	5.92
1278.434	2010	1000	446	3.73
1297.155	1330	03 <sup>1</sup> 0 03 <sup>3</sup> 0	446	0.390
1300.791	2110	1110	446	0.364
1285.589 1280.5	21 <sup>1</sup> 0 10 <sup>0</sup> 0 11 <sup>1</sup> 0	0000	446	0.412
1286.4	1110	0110	456 456	3.15 0.354
1269.894	1020	0000	546	3.15
1277.760	1110	0110	546	0.362
1247.9	10 <sup>0</sup> 0	0000	448	1.75
1255.7	1110	0110	448	0.200
1265.5	1000	00 <sup>0</sup> 0	447	0.350
1634.989	00 <sup>0</sup> 1	01 <sup>1</sup> 0	446	0.231
1749.058	0310	00 <sup>0</sup> 0	446	0.200
1880.268	1120	00 <sup>0</sup> 0	446	1.41
1886.018	12 <sup>2</sup> 0	0110	446	0.156
1873.231	1201	0110	446	0.053
1974.571	20 <sup>0</sup> 0	01 <sup>1</sup> 0	446	SQ = 0.024
2181.66	06 <sup>0</sup> 0	1000	446	See Note B

Table 14.  $N_2O$  Band Intensities (Contd)

Band Center	Upper	Lower	Isotope	S <sub>v</sub> at 296K
$\nu_{\rm c}$	Level	Level	1	(Multiply by 10 <sup>-20</sup>
(cm <sup>-1</sup> )			ì	Molecules 1 cm <sup>2</sup> cm <sup>-1</sup> )
(0111 /			<u> </u>	Molecules Cili Cili /
2223.756	0001	0000	446	5023.
2209.523	00 <sup>0</sup> 1 01 <sup>1</sup> 1	0110	446	568.
2195.840	l 02 <sup>0</sup> 1		446	16.8
2195.387	0221	0200 02 <sup>2</sup> 0	446	31.8
2195.914	1001	1000	446	10.1
2182,200	10 <sup>0</sup> 1 03 <sup>1</sup> 1 03 <sup>3</sup> 1	03 <sup>1</sup> 0 03 <sup>3</sup> 0	446	1.958
2181,386	0371	0370	446	1.88
2181.711	11/1	1110 00°1 00°0 0110	446	1.10
2193.623	00°2 00°1	0001	446	0.201
2177.659	0111	0010	456	18.1
2164.13	0001	0000	456	2.04
2201.604 2187.389	0111	00 <sup>0</sup> 0 01 <sup>1</sup> 0	546	18.1
2107.309	01 1	01.0	546	2.10
2218.97	0001	00°0	448	10.1
2204.70	l 01 1	0110	448	1.15
2221.3	0001	0000	447	2.01
2207.25	0001 011	01 <sup>1</sup> 0 00 <sup>0</sup> 0 01 <sup>1</sup> 0	447	0.234
	1			
2322.624	040	00°0	446	2.11
2309.109	05 <sup>1</sup> 0	0110	446	0.54
0.404.000	1000	00°0		
2461.998	12 <sup>0</sup> 0 13 <sup>1</sup> 0 14 <sup>0</sup> 0 14 <sup>2</sup> 0	0010	446	27.6
2457.446	13.0	0110	445	4.68
2452.807 2453.851	1420	0220	446	0.239
2463.345	2200	02 <sup>0</sup> 0 02 <sup>2</sup> 0 10 <sup>0</sup> 0	446	0.321
2403.043		10 0	446	0.192
2563.341	20 <sup>0</sup> 0	0000	446	120.
2577.090	21 <sup>1</sup> 0	0110	446	12.2
2580.118	22 <sup>0</sup> 0 22 <sup>2</sup> 0	02 <sup>0</sup> 0 02 <sup>2</sup> 0	446	0.348
2588.310	2220	0220	446	0.648
2551.466	3000	10 <sup>0</sup> 0 00 <sup>0</sup> 0	446	0.696
2534.21	2000	0000	546	0.454
2554.3	20 <sup>0</sup> 0	00°0 00°0	456	0.384
2491.3	20 <sup>0</sup> 0	00~0	448	0.192
2474.785	12 <sup>2</sup> 0	00 <sup>0</sup> 0	446	See Note A
2798.290	0111	0000	446	8.06
2775.207	0221	0110	446	0.401
2784.370	0221	0110	446	0.912
2763.124	02 <sup>2</sup> 1 03 <sup>1</sup> 1	0200	446	0.025
2753.508	l 03 <sup>1</sup> 1	0220	446	0.020
2770.594	0331	0220	446	0.078
	]	0-		
3363,974	0201	00 <sup>0</sup> 0	446	8.82
3342.491	0311	0110	446	1.57

Table 14. N<sub>2</sub>O Band Intensities (Contd)

Band Center	Upper	Lower	Isotope	S <sub>v</sub> at 296K
$\nu_{\rm c}$	Level	Level		(Multiply by 10 <sup>-20</sup>
(cm <sup>-1</sup> )				Molecules -1 cm <sup>2</sup> cm -1)
(0.11. /				
3480.821	10 <sup>0</sup> 1	00 <sup>0</sup> 0	446	173.
3473.212	1111	$01^{1}0$	446	19.24
3462.030	1201 1221 2001 1001	0200	446	0.563
3464.713	1221	02 <sup>2</sup> 0 10 <sup>0</sup> 0	446	1.064
3445.921	2001	1000	446	0.652
3443.659	1001	0000	546	0.627
3430.95	10 <sup>0</sup> 1	00°0	456	0.627
3439.1	1001	.00-0	448	0.348
3466.54	06 <mark>0</mark> 0	00 <sup>0</sup> 0	446	See Note B
3474.65	0620	0000	446	See Note A and B
0414,00				See Note II and B
3748.252	.22 <mark>0</mark> 0	00°0	446	3.52
3747.031	2310	01 10	446	0.512
0000 044	14 <sup>0</sup> 0	a à 0 a	440	0.400
3620.941	14-0	00°0	446	0.492
3836.373	30 <sup>0</sup> 0	0000	446	7.28
3857.612	3110	0110	446	0.698
00011012				
4061.979	11 <sup>1</sup> 1	00 <sup>0</sup> 0	446	0.092
	1_	0-		
4335.798	23 <sup>1</sup> 0	00°0	446	0.083
4417.379	0002	0000	446	6.07
4388,928	0112	0110	446	0.686
1000,020	01 5	01 0	440	0.000
4630.164	1201	0000	446	0.597
4500 000	220.	2000		
4730.828	20 <sup>0</sup> 1 21 <sup>1</sup> 1	00 <sup>0</sup> 0 01 <sup>1</sup> 0	446	3.90
4730.408	21-1	01-0	446	0.410
4977.695	0112	. 00°0	446	0.058
.511.000			170	0.000
5026.34	3200	0000	446	0.255
5105.65	40 <sup>0</sup> 0	00 <sup>0</sup> 0	446	0.255
				,

The intensities of the majority of the bands have been calculated from the experimental values for the entire band systems listed in Table 13. Calculating the intensity of an individual band from that of the entire band system involves the population of each energy level, the degeneracy of each level, and the relative transition probabilities.

In some of the band systems, the experimental results indicate that the transition probabilities are the same for all bands within a given system. However, as in the  $12^{0}$ 0 band system, for example, the transition probabilities are greater for the  $13^{1}0 \leftarrow 01^{1}0$  and  $14^{0}0 \leftarrow 02^{0}0$  bands than for the  $12^{0}0$  band. These differences in transition probabilities were found experimentally by comparing the relative intensities of several isolated lines within the system.

Equations relating the intensities of individual lines to that of the entire band are given in Section 3. These are applicable to the  $N_2O$  bands listed in Table 14 with the exception of two forbidden  $\Delta \leftarrow \Sigma$  bands,  $02^2O$  and  $12^2O$ , and those listed in Table 15. The factor  $\zeta$  (see Section 3 Eq. (13)) that accounts for the Coriolis vibration-rotation interaction can be assumed to be zero for all bands in Table 14, except for the  $03^1O$  and  $11^1O$  bands;  $\zeta$  equals approximately -0.01 and -0.007, respectively, for these bands.

Young (1972) has tabulated the relative intensities of the lines within a given band for which the Coriolis interaction is negligible. A large fraction of the intensity of a band system is in the main band; therefore, uncertainties in the relative transition probabilities within a band system do not seriously increase the uncertainty of the main-band intensity calculated on the basis of that of the entire band system. Thus, the percent of uncertainty in the intensity of the main band is approximately the same as that for the entire band system, whereas the uncertainty for the hot bands may be greater.

#### 4.4.3 FORBIDDEN BANDS AND PERTURBED LINES

A few rotational levels of the  $06^{\circ}0$  vibrational state (centered at J=46) and the  $06^{\circ}0$  state (centered at J=28) are perturbed by the corresponding levels of the  $10^{\circ}1$  state to such an extent that the normally very weak lines "borrow" enough

Line	Band	ν <sub>ο</sub> (cm <sup>-1</sup> )	$S_{\rm J}$ $\times 10^{-20}$ molecules $^{-1}$ ${\rm cm}^2$ cm $^{-1}$
R45	10 <sup>0</sup> 1	1)3508.v30	0.207
R45	06 <sup>0</sup> 0	2)3508.186	0.046
P47	$10_{06}^{0}$ 1	1)3430.230	0.136
P47		2)3430.400	0.031
R27	10 <sup>0</sup> 1	1)3500.040	2.11
R27	06 <sup>2</sup> 0	2)3499.970	0.0233
P29	10 <sup>0</sup> 1	1)3452.330	1.71
P29	06 <sup>2</sup> 0	2)3452.260	0.0188
R45	$\begin{array}{c} 10^{0}1 \leftarrow 10^{0}0 \\ 10^{0}1 \leftarrow 10^{0}0 \end{array}$	3)2226.713	0.0118
P47		3)2149.246	0.0042

Table 15. Parameters of Perturbed Lines of N2O

- 1) The perturbed line positions of the 10<sup>0</sup>1 band are from observed values by Tidwell et al. (1960).
- 2) The calculated positions of perturbed lines of the 06<sup>0</sup>0 and 06<sup>2</sup>0 bands were determined from known perturbed positions of the 10<sup>0</sup>1 lines and Toth's (1971a) values of the line separations.
- 3) The calculated positions of the perturbed  $10^{01} 10^{00}$  lines were determined from Toth's (1971a) results and the positions of the unperturbed lines calculated on the basis of the constants in Table 12.
- 4) The perturbed line intensities of the  $06^{\circ}0$  and  $06^{\circ}0$  bands are based on the intensities of the unperturbed lines of the  $10^{\circ}1$  band and Toth's (1971a) results. The unperturbed line intensities of the  $10^{\circ}1$  and  $10^{\circ}1 \leftarrow 10^{\circ}0$  bands are based on the band intensities given in Table 13 and Young's (1972) relative line intensities.

intensity from the  $10^{0}1$  lines to appear, at the same time shifting the positions of the lines related to these rotational levels (Toth, 1971a). The resulting positions and intensities of the affected lines have been calculated separately and are given in Table 15. The R27 and R29 lines of the  $10^{0}1 - 10^{0}0$  band are not listed in the table because the changes in their intensities and positions are negligible.

## 4.4.4 LINE HALF-WIDTHS

Several workers have measured the half-widths of  $N_2O$  lines broadened by  $N_2$ , which is a good approximation to broadening by air. Toth (1971b) has recently measured the widths of lines in the R branches of the  $10^O$ 1 and  $02^O$ 1 bands directly from observed spectra with a small correction for the effect of the spectrometer slitwidth. Margolis (1972) has used the same method to measure the lines in both the P- and R-branches of the  $00^O$ 2 band. The results of these two workers are in

good agreement, indicating that there is little, if any, dependence on vibrational mode. Lowder's (1972) recent measurements on the  $00^{\circ}1$  band show approximately the same dependence on J as do the results of Toth and Margolis, although Lowder's values averaged approximately 10 percent less. Oppenheim and Goldman (1971) have measured half-widths indirectly by applying band models to low-resolution spectra of a wide variety of N<sub>2</sub>O samples. Their results are in fair agreement with those of Margolis and Toth. Fraley et al, (1962) reported an average value of 0.05 cm<sup>-1</sup> atm<sup>-1</sup> for lines in the  $00^{\circ}1$  band; this value is considerably lower than those reported by the workers mentioned above.

We have adopted half-widths of  $N_2$ -broadened lines reported by Toth (1971b) to be used for atmospheric  $N_2$ O lines near  $296^{\circ}$ K. A few values are listed in the tabulation below; values for other J's can be found by interpolation and for other temperatures by assuming the half-widths are inversely proportional to the square root of temperature.

J	o cm -1 atm -1
1	0.0915
4	0.0948
10	0.0892
20	0.0812
30	0.0767
40	0.0748
50	0.0698
60	0.0604

#### 4.5 Carbon Monoxide

For the CO bands, we have depended heavily on the work of Young (1968). Table 16 provides the rotational constants which were used to compute the line positions of the main isotope. The positions of the less abundant isotopes were computed from the appropriate constants for the 26 isotope by applying the ratio of reduced masses. The accuracy of the line positions in the main isotope is expected to be about  $\pm$  0.001 cm<sup>-1</sup>. The accuracy of the line positions of the other isotopes will be somewhat less, about  $\pm$  0.01 cm<sup>-1</sup>.

The intensities for the fundamental and first two overtone bands were taken from Young and are reproduced in Table 17. The intensities for the isotopic bands were taken to be the same as for the 26 isotope reduced by the relative abundances given in Table 4 and the square of the frequency. The intensity of the fundamental appears to be known very accurately, perhaps within  $\pm$  2 percent; the first overtone is less accurately known to  $\pm$  10 percent; and the second overtone is known to  $\pm$  4 percent (see Young and Eachus, 1966); Burch and Gryvnak (1967). Half-width values have been added to the compilation following the work of Hunt et al, (1968).

Symbol	Value
$\omega_{\mathbf{e}}$	2169.836
$egin{array}{l} \omega_{\mathbf{e}} & & & \\ \omega_{\mathbf{e}} \mathrm{X}_{\mathbf{e}} & & & \\ \omega_{\mathbf{e}} \mathrm{Y}_{\mathbf{e}} & & & & \end{array}$	13.295
$\omega_{\mathbf{e}}^{\mathbf{v}}\mathbf{Y}_{\mathbf{e}}^{\mathbf{c}}$	0.0115
$\mathbf{B}_{\mathbf{e}}^{*}$	1.931285
Be αe γe Dc	0.017535
γ <sub>e</sub>	1.01x10 <sup>-5</sup>
$\mathbf{D_{c}^{r}}$	$6.12 \times 10^{-6}$
$\mathcal{B}_{\mathbf{a}}^{-}$	1.0x10 <sup>-9</sup>

Table 16. Rotational Constants Used in the Calculation of CO Line Positions

Table 17. Intensities of CO Bands

	1-0	2-0	3-0
Intensity, S(cm <sup>-1</sup> /molecule-cm <sup>-2</sup> )	9.70x10 <sup>-18</sup>	6.99x10 <sup>-20</sup>	4.83x10 <sup>-22</sup>

#### 4.6 Methane

This molecule is a spherical top, in the rigid rotor approximation. It has tetrahedral  $(T_d)$  symmetry in the rest configuration of its nuclei. Rotation-vibration interactions are complicated even for its simplest infrared-active bands. Starting from the molecular Hamiltonian and the electric dipole-moment operator, transition energies, selection rules, and intensities may be calculated. However, the techniques and the results are complex, and it is not convenient to summarize them here. Therefore, the user is referred to the original papers on this subject John (1968), Schaffer et al. (1939), Hecht (1960), Moret-Bailly (1961), Herranz (1961), Fox (1962), Dang-Nhu (1969), and Susskind (1972).

For the purpose of the present data compilation, we have established the following conventions in notation. The isotopic species  $^{12}\mathrm{CH}_4$ ,  $^{13}\mathrm{CH}_4$ , and  $^{12}\mathrm{CH}_3\mathrm{D}$  are denoted by the digits 211, 311, and 212, respectively, in columns 75 through 77. The quantum numbers for the initial and final states of a transition are specified in columns 36 through 69 as follows:

$$v_1'v_2' \ell_2'v_3' \ell_3' v_4' \ell_4' \ell' \quad v_1''v_2' \ell_2'v_3' \ell_3'v_4' \ell_4' \ell' \quad \text{J'R'} \quad \text{C'} \quad \text{N'} \quad \text{J''R''} \quad \text{C''} \quad \text{N''} \quad \text{IX} \\ 1X \quad 811 \quad 1X \quad 811 \quad 1X \ 212 \ 1A1 \ 111 \ 111 \ 1X \ 212 \ 1A1 \ 111 \ 111 \\ \text{except for type E symmetry which has for C the format 1X 1A1 instead of 1A1 1I1.} \\ \text{The initial and final state vibrational and rotational quantum numbers have their usual meanings.} \quad \text{To avoid ambiguity, we establish some further conventions for the present data compilation.} \quad \text{The selection rule C'} \leftarrow \text{C''} \text{ on } T_d \text{ symmetry is always taken to be}$$

 $A_1 - A_2$ ,  $A_2 - A_1$ , E - E,  $F_1 - F_2$ , or  $F_2 - F_1$ . The numbering scheme for the N's

begins with 1, 2, 3 . . . Whenever possible, N increases with increasing groundstate energy; the stronger lines correspond to the selection rule,  $N^{1} - N^{11} = 0$ .

This section describes methane spectral data in the 3 to 8.5  $\mu$ m region. The following bands, as summarized in Table 18, have been included:  $\nu_2$ ,  $\nu_3$ ,  $\nu_4$ ,  $\nu_2$ +  $\nu_4$ ,  $2\nu_4$ .

Table 18. Methane Bands Included in Data Compilatio
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Isotope	Band	Center (cm <sup>-1</sup> )	Upper State	Lower State	Intensity (cm <sup>-1</sup> /mole-cm <sup>-2</sup> )
311	$\nu_4$	1297.88 <sup>a</sup>	00000111	00000000	6.59x10 -20h
211	$\nu_4$	1305.9138 <sup>b</sup>	00000111	00000000	5.87x10 <sup>-18i</sup>
211	ν <sub>2</sub>	1533.289 <sup>C</sup>	01100001	00000000	8.91x10 <sup>-20i</sup>
311	ν <sub>3</sub>	3009.53 <sup>d</sup>	00011001	00000000	1.36x10 <sup>-19h</sup>
211	ν <sub>3</sub>	3018.9205 <sup>e</sup>	00011001	00000000	1.21x10 <sup>-17i</sup>
211	244	2600 <sup>f</sup>	00000222	00000000	1x10 <sup>-19j</sup>
211	ν <sub>2</sub> + ν <sub>4</sub>	2818, 2838 <sup>g</sup>	01100112	00000000	8x10 <sup>-19h</sup>

- a. Kyle et al, (1970)
- b. Michelot and Fox (1973)
- c. Dang-Nhu (1968)
- d. McDowell (1966)
- Bobin and Fox (1973)
- Fox (1973)
- Benedict (1973)
- h. 1/89 times value for corresponding band of 211 isotope
- i. Armstrong and Walsh (1960)
- j. 1/100 times value for  $\nu_3$  of 211 isotope k. 1/15 times value for  $\nu_3$  of 211 isotope

It is planned to add other weak but significant bands in this spectral region at a later time.

Many line positions, together with their absolute intensities and widths, have been included in the present data compilation, even though the corresponding quantum number assignments are uncertain or unknown at this time. It must be stressed that much of the needed theoretical and experimental research on spectra of methane is still incomplete. Consequently, a large portion of the data compilation should be considered tentative and subject to revision at a later time.

#### 4.6.1 LINE POSITIONS

The band  $\nu_3$  at 3.3  $\mu$ m is the strongest infrared-active vibration-rotation fundamental of CH<sub>4</sub>. High-resolution measurements of line positions for  $^{12}$ CH<sub>4</sub> in the range 2884 to 3141 cm<sup>-1</sup> have been used. See Henry et al, (1970), and Barnes et al, (1972). Quantum number assignments for the allowed lines from 2840 to 3167 cm<sup>-1</sup> were made by Bobin and Fox (1973) on the basis of fourth-order perturbation theory. Some forbidden lines were assigned by Barnes et al, (1972) using third order theory. Spectroscopic parameters determined for the ground-state and for  $\nu_3$  of CH<sub>4</sub> are listed in Tables 19 and 20, respectively. The corresponding band of the isotopic species  $^{13}$ CH<sub>4</sub> has been measured from 2873 to 3123 cm<sup>-1</sup>. The assignments of McDowell (1966) with some modifications were used. The corresponding spectroscopic parameters are listed in Table 23.

Table 19.	Spectroscopic	Parameters	for	Ground	State	of	<sup>12</sup> CH₄
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Parameter	Value (cm <sup>-1</sup> )
В	5.24059 <u>+</u> 0.00006 <sup>a</sup>
D <sub>s</sub>	(1.086+0.003)x10 <sup>-4a</sup>
$D_{t}$	(4.403 <u>+</u> 0.099)x10 <sup>-6b</sup>

- a. Barnes et al, (1972)
- b. Ozier et al, (1970). The error bar is derived from the values given by Barnes et al, (1972) and Husson and Dang Nhu (1971).

The band at 7.7  $\mu$ m is the next strongest fundamental of  $^{12}$ CH<sub>4</sub>. High-resolution measurements in the 1225 to 1393 cm<sup>-1</sup> range made by Botineau (1972) were used to obtain spectral line positions. Quantum-number assignments for the allowed lines, to J=12 for the R and Q branches, and J=13 for the P branch, were made by Michelot and Fox, (1973) on the basis of a fourth order calculation. For J=13 to 15 in the Q branch only, and for some J=13 R-branch lines, quantum-number assignments were taken from the work of Husson and Poussigue (1971). No forbidden lines of this band have been included in the data compilation yet. The determined spectroscopic parameters are given in Table 21. For  $\nu_4$  of  $^{13}$ CH<sub>4</sub>, the measurements of Kyle et al, (1970), extend from 1226 to 1359 cm<sup>-1</sup>, and possibly further. The assignments of Kyle et al, (1970) with some modifications were used; spectroscopic parameters appear in Table 24.

Table 20.	Spectroscopic	Parameters*	for	ν <sub>3</sub>	of	<sup>12</sup> СН <sub>4</sub>
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Parameter	Value (cm <sup>-1</sup> )	Parameter	Value (cm <sup>-1</sup> )
m n p q s t x v	3018.9205 9.87157 -4.0622x10 <sup>-2</sup> -2.959x10 <sup>-4</sup> 4.329x10 <sup>-5</sup> 1.942x10 <sup>-7</sup> -9.11x10 <sup>-8</sup> -4.7921x10 <sup>-2</sup> 3.622x10 <sup>-5</sup>	g h k <b>£</b> j u z z' z'	4.265x10 <sup>-3</sup> 8.365x10 <sup>-5</sup> -1.925x10 <sup>-5</sup> 2.509x10 <sup>-7</sup> 5.84x10 <sup>-8</sup> 2.605x10 <sup>-5</sup> -5.39x10 <sup>-8</sup> 1.49x10 <sup>-6</sup> 7.08x10 <sup>-8</sup>

\*Bobin and Fox (1973)

Table 21. Spectroscopic Parameters\* for  $v_4$  of  $^{12}\mathrm{CH}_4$ 

Parameter	Value (cm <sup>-1</sup> )	Parameter	Value (cm <sup>-1</sup> )
m n p q s t x v	1305.9138 5.5752 -6.4192x10 <sup>-2</sup> 1.91x10 <sup>-3</sup> 1.479x10 <sup>-6</sup> -1.11x10 <sup>-6</sup> -1.79x10 <sup>-8</sup> -5.2263x10 <sup>-2</sup> 2.319x10 <sup>-5</sup>	g h k <b>l</b> j u z z' z'	1.8643x10 <sup>-2</sup> 6.590x10 <sup>-4</sup> 2.88x10 <sup>-6</sup> 1.67x10 <sup>-7</sup> -3.78x10 <sup>-9</sup> 2.077x10 <sup>-5</sup> -1.18x10 <sup>-8</sup> -1.901x10 <sup>-6</sup> 8.28x10 <sup>-8</sup>

\*Michelot and Fox (1973)

The  $\nu_2$  fundamental at 6.5  $\mu$ m is relatively weakly infrared-active, by virtue its Coriolis interaction with  $\nu_4$ . Quantum-number assignments are based on the results of Dang Nhu (1969) who developed a fourth-order theory and applied it to unpublished spectra of moderately high resolution. Spectroscopic parameters are listed in Table 22.

High-resolution spectra of  $\nu_2$ +  $\nu_4$  and 2  $\nu_4$  are available in the region of approximately 2450 to 3200 cm<sup>-1</sup> (Plyler et al, 1960; and Hall, 1973). Quantum-number assignments for 2  $\nu_4$  have been made on the basis of a third-order theoretical analysis. A partial analysis of  $\nu_2$ +  $\nu_4$  has been done in analogy with the quantum-number assignments in the work of (Bregier, 1970; and Hilico, 1970), on  $\nu_2$ +  $\nu_3$ . Spectroscopic parameters for  $\nu_2$ +  $\nu_4$  and 2  $\nu_4$  are given in Tables 25 and 26 respectively.

Table 22. Spectroscopic Parameters\* for  $\nu_2$  of  $^{12}{\rm CH}_4$ 

Parameter	Value (cm <sup>-1</sup> )
v <sub>2</sub>	1533.289
B <sub>2</sub>	5.319
B <sub>0</sub>	5.230
d <sub>2</sub>	5.7x10 <sup>-5</sup>
d <sub>0</sub>	2.1x10 <sup>-5</sup>
z <sub>2</sub>	2.9x10 <sup>-2</sup>
f <sub>2</sub>	-5.2x10 <sup>-3</sup>
e <sub>2</sub>	-2.8x10 <sup>-5</sup>
e <sub>0</sub>	-5.0x10 <sup>-6</sup>

\*Dang Nhu (1968)

Table 23. Spectroscopic Parameters\* for  $\nu_3$  of  $^{13}\mathrm{CH}_4$ 

Parameter	Value (cm <sup>-1</sup> )
$\nu_{\rm O}^{-2({ m B}\zeta_3){ m eff}}$	3009.05 <u>+</u> 0.03
$B_0^{+B_{eff}^{P,Q}-2(B\zeta_3)_{eff}}$	9.963+0.004
Beff-Bo	-0.0386 <u>+</u> 0.0008
2(D <sub>0</sub> +D <sub>1</sub> )	(4.2±0.4)x10 <sup>-4</sup>
D <sub>o</sub> -D <sub>1</sub>	$(2.1\pm0.5)\times10^{-5}$
<b>6</b> <sub>3</sub>	0.046+0.005
$D^{JT}$	(4.7±2.8)x10 <sup>-5</sup>
$\mathbf{d}^{\mathbf{J^{ au}}}$	$(5.4\pm1.7)\times10^{-5}$

\*McDowell (1966)

Table 24. Spectroscopic Parameters\* for  ${m v}_4$  of  $^{13}{
m CH}_4$ 

Parameter	Value (cm <sup>-1</sup> )
ν <sub>4</sub> Β' Β' D ξ F <sub>4s</sub> t <sub>044</sub> t <sub>134</sub> t <sub>224</sub>	$1297.88+0.02$ $5.179+0.005$ $5.194+0.005$ $(1.16+0.02)\times10^{-4}$ $0.477+0.005$ $(2.26+0.02)\times10^{-3}$ $-4.5\times10^{-6}$ $(4.84+0.02)\times10^{-4}$ $(-1.46+0.01)\times10^{-2}$

\*Kyle et al, (1970)

Table 25. Spectroscopic Parameters\* for  $\nu_2$ +  $\nu_4$  of  $^{12}{\rm CH}_4$ 

Parameter	Value (cm <sup>-1</sup> )
ν <sub>o</sub> (Q)	2818, 2838

<sup>\*</sup>Hiliev (1970) - Further analysis, including that of the interaction between  ${\rm F_1}$  and  ${\rm F_2}$  substates, is necessary in order to obtain more complete values of spectroscopic parameters.

Table 26. Spectroscopic Parameters\* for 2  ${m \nu}_4$  of  $^{12}{
m CH}_4$ 

Parameter	Value (cm <sup>-1</sup> )
ε Β Βζ D G <sub>44</sub> g h	$ \begin{array}{r} 2600.29 \\ 5.175 \\ 2.520 \\ 1.0x10^{-4} \\ 3.1 \\ 1.837x10^{-2} \\ 6.579x10^{-4} \end{array} $

\*Fox (1962)

#### 4.6.2 LINE INTENSITIES

Although it is recognized that it would be desirable to include in the data compilation all methane lines whose absolute intensity exceeds the cutoff specified in Table 3, it has not been possible to achieve this goal because of present experimental and theoretical limitations.

Absolute intensities for the allowed lines in  $\nu_3$  of  $^{12}\mathrm{CH}_4$  were calculated, starting from the measured values for R(0); R(1), and R(2). The relative intensities of forbidden lines (Barnes et al, 1972) were used for calculating their absolute intensities. The absolute line intensities for  $\nu_3$  of  $^{13}\mathrm{CH}_4$  were calculated on the basis of those for  $\nu_3$  of  $^{12}\mathrm{CH}_4$ , together with the terrestrial  $^{12}\mathrm{C}/^{13}\mathrm{C}$  ratio (see Table 4). Calculated and/or measured absolute band intensities are listed in Table 18.

Absolute line intensities for  $\nu_4$  have been calculated on the basis of the measured values for R(0), R(1), and R(2). For  $^{13}{\rm CH_4}$ , absolute intensities were calculated as for  $\nu_3$ . Absolute band intensities are given in Table 18.

Absolute line intensities for  $\nu_2$ , have been calculated on the basis of theoretical relative-line intensities and the experimental absolute band intensity in Table 18.

Absolute-line intensities for  $\nu_2$ + $\nu_4$  were determined from the solar spectra of Hall (1972), with an assumed CH<sub>4</sub> air mass of approximately  $4 \text{x} 10^{19}$  molecules/cm<sup>2</sup> and an assumed temperature of  $273^{\circ}$ K and a pressure of 0.65 atm.

Absolute line intensities for  $2\nu_4$  were calculated from the relative intensity formula of Fox (1962) together with the absolute band intensity in Table 18. The latter intensity was taken to be approximately 1/100 of that for  $\nu_3$  of  $^{12}\mathrm{CH}_4$ .

#### 4.6.3 LINE WIDTHS

The J- and T-dependence of methane line widths is taken from the results of Varanasi et al, (1971, 1972) and Tejwani and Varanasi (1971). The only measured values of air-broadened CH<sub>4</sub> half-widths are for multiples of  $\nu_3$  and  $2\nu_3$  at T= 295°K. For J≈1 to 5,  $\gamma^0\approx 0.061$  cm <sup>-1</sup> atm <sup>-1</sup>; for J≈15 to 17,  $\gamma^0\approx 0.048$  cm <sup>-1</sup> atm <sup>-1</sup>. These results agree with values calculated from  $\gamma^0$  for CH<sub>4</sub>-0<sub>2</sub>, assuming N<sub>2</sub> and 0<sub>2</sub> with their partial pressures in air. Measurements and calculations of  $\gamma^0$  for CH<sub>4</sub>-H<sub>2</sub> in  $\nu_4$  suggest, but do not prove directly, that  $\gamma^0$  may be independent of vibration-rotation band. For the purpose of the present data compilation, we adopt the value  $\gamma^0=0.055$  cm <sup>-1</sup> atm <sup>-1</sup> for all CH<sub>4</sub> lines. There are no results available for the T-dependence of  $\gamma^0$  for CH<sub>4</sub>-air or even CH<sub>4</sub>-N<sub>2</sub> or CH<sub>4</sub>-0<sub>2</sub> broadening. From the calculations and measurements for CH<sub>4</sub>-H<sub>2</sub> broadening with T, we assume the usual T<sup>-1/2</sup> dependence. In conclusion, for the present data compilation, we use

$$\gamma^{\circ} = 0.055 \left(\frac{296}{T}\right)^{1/2} \left(\frac{p}{1 \text{ atm}}\right).$$
 (16)

#### 4.7 Oxygen

The infrared atmospheric bands of oxygen have been interpreted by Van Vleck as magnetic dipole transitions between intersystem electronic combinations, a singlet-triplet transition  $a^1 \Delta_g \leftarrow X^3 \tilde{\Sigma_g}$ . The  $\Delta$  v=0 (0,0) band at 7882.39 cm<sup>-1</sup> (1.27  $\mu$  m) has an Einstein A coefficient of 1.9x10<sup>-4</sup> sec<sup>-1</sup> Jones and Harrison (1958). The (0,0) band, and the weaker (1,0) band at  $9365.89 \text{ cm}^{-1}$  have been observed in terrestial atmospheric absorption by Herzberg and Herzberg (1947). The (0.1) band at  $6325.99~
m cm^{-1}$  has been observed in the twilight airglow emission by Jones and Harrison (1958). In addition to these bands there is an electric quadrupole  $(b_{\Sigma}^{1}{}_{\sigma}^{-}a^{1}\Delta_{\sigma})$  transition at 1.908  $\mu$ m that has been detected in the emission spectrum of a discharge through 02 and helium (Noxon, 1961). Finally, submillimeterwave rotational transitions (McKnight and Gordy, 1968) and spin reorientation spectra (Zimmerer and Mizushima, 1961) at 60 GHz have been observed in the ground electronic state. The (a-X) system and the microwave spectra are discussed below. The atmospheric "A" band at 7619A, representing the magnetic dipole transition b  $\Sigma_{\sigma}^{+}$   $X^{3}$   $\Sigma_{\sigma}^{-}$ , is also included (Wark and Mercer, 1965; Burch and Gryunak, 1967).

With the molecular rotational momentum designated by K and the electronic spin vector by S, the total angular momentum J is given by

$$J=K+S$$
.

Thus, for the singlet-delta state J=K, and the energy levels, apart from the vibration, are given by

$$F = B_{v}K(K+1) - D_{v}K^{2}(K+1)^{2}, (17)$$

where  $B_{\mathbf{v}}$  is the rotational constant and  $D_{\mathbf{v}}$  is the first order centrifugal distortion constant for the particular vibrational state. The constants for this state, obtained from measurements of the infrared bands, are listed in Table 27.

The expressions for the rotational energies of the rho-type triplet are obtained from a solution of the Hamiltonian (West and Mizushima, 1966):

$$H = B K^{2} + \frac{2}{3} \lambda (3S_{z}^{2} - S^{2}) + \mu K \cdot S,$$
 (18)

where  $\lambda$  is the spin-spin interaction coupling constant and  $\mu$  is the spin-rotation interaction coupling constant.

Constant	Value (in cm <sup>-1</sup> )
Bo	1.41783 1.4007 4.86x10 <sup>-6</sup>

Table 27. Constants of the  $^{1}\Delta_{g}$  State of  $^{0}2$  (Herzberg and Herzberg, 1947)

Centrifugal stretching effects are approximately corrected for by assuming a K(K+1) dependence for B,  $\lambda$  and  $\mu$ , namely:

$$B = B_{v} - D_{v}K(K+1) + H_{v}K^{2}(K+1)^{2},$$

$$\lambda = \lambda_{o} - \lambda_{1}K(K+1), \text{ and}$$

$$\mu = \mu_{o} - \mu_{1} K(K+1).$$
(19)

For each value of the quantum number at end-over-end rotation, K, the triplet energies are given by  $F_1(K)$ ,  $F_2(K)$ , and  $F_3(K)$  where J=K+1, J=K and J=K-1, respectively. Both  $F_1(K)$  and  $F_3(K)$  average about 2 cm<sup>-1</sup> lower than the  $F_2(K)$  component. Values for the constants of the triplet-sigma state, obtained from both infrared and microwave measurements, are given in Table 28.

The band centers are given by

$$G(v',v'') = \mathbf{p}_{e} + \omega_{e}'(v'+1/2) - \omega_{e}'x_{e}'(v'+1/2)^{2} + \dots - \omega_{e}''(v''+1/2) + \omega_{e}''x_{e}''(v''+1/2)^{2} - \omega_{e}'y_{e}'(v''+1/2)^{3} + \omega_{e}''z_{e}''(v''+1/2)^{4} + \dots,$$
(20)

where the prime and double primes refer to the singlet and triplet states respectively.

The selection rules for magnetic dipole radiation are

$$\Delta J = 0, + 1$$

and

$$+ \leftrightarrow +$$
,  $- \leftrightarrow -$ ,  $g \leftrightarrow g$ ,  $u \leftrightarrow u$ .

Table 28.	Constants	for the	$^{3}\Sigma_{g}$	State	of	02
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Constant	Reference	Value (cm <sup>-1</sup> )
B <sub>0</sub> B <sub>1</sub>	a	1.4376809
$B_1$	b	1.421979
D <sub>0</sub>	b	$4.913 \times 10^{-6}$
$D_1^0$	b	$4.825 \times 10^{-6}$
Do Do H	b	$3.0 \times 10^{-10}$
$\lambda_0^0$	c	1.9847530
$\lambda_1^0$	c	$-1.950 \times 10^{-6}$
	c	$-8.42930 \times 10^{-3}$
$\begin{smallmatrix} \mu_{\mathbf{O}} \\ \mu_{1} \end{smallmatrix}$	c	8.01×10 <sup>-9</sup>
$\omega_{\mathbf{e}}$	b	1580.3613
$\omega_{\mathbf{e}}^{\mathbf{e}}\mathbf{x}_{\mathbf{e}}$	b	12.0730
$\omega_{\mathrm{e}} \mathrm{y}_{\mathrm{e}}$	b	$5.46 \times 10^{-2}$
$\omega_{27}$	b	$-1.43 \times 10^{-3}$
$\Delta G_{1/2}$	b	1556.3856

- a. McKnight and Gordy (1968)
- b. Babcock and Herzberg (1948)
- c. West and Mizushima (1966)

The possible branches and the nomenclature used here for the  ${}^1\Delta_g - {}^3\Sigma_g^-$  transition are shown in Table 27. Since the oxygen-16 nuclei obey Bose-Einstein statistics, only the positive rotational levels occur. In the ground state this causes an alternation of lines such that only odd values of the rotational quantum number K are present. For the heteronuclear isotopes of oxygen, however, all rotational levels occur; the  $0^{17}0^{17}$  molecule has alternate rotational levels with nuclear statistical weights of 5 and 7 (Gordy et al, 1953). In  $0^{16}0^{16}$  (and  $0^{18}0^{18}$ ) there are four branches with  $\Delta K$ =+1, three with  $\Delta K$ =0, and two with  $\Delta K$ =+2, the latter branches being designated by superscripts S and 0. On the magnetic tape the six quantum numbers of the transition, v', J', K', v'', J'', K'', are given in the field of columns 38 through 62. In addition, the nine branches are listed in columns 64 and 65 with the superscript, representing the  $\Delta K$  of the transition, preceding the  $\Delta J$  designation. A diagram indicating the transitions involved in the  ${}^1\Delta_g + {}^3\Sigma_g^-$  band is given in Figure 1.

The above description generally applies to the microwave transitions of pure rotation and transitions between levels of the triplet state. In the latter the labelling is given as K+ and K-, designating the transitions  $F_2(K) - F_1(K)$  and  $F_2(K) - F_3(K)$  respectively. Intensities have been calculated (see Townes and Schawlow, 1955). A good summary of the various bands of oxygen molecule can be found in the recent review article by Krupenie, 1972.

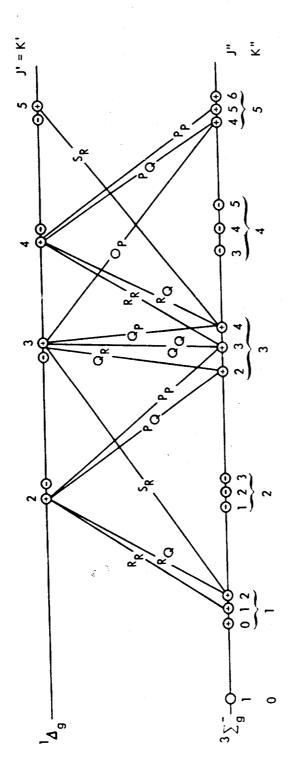


Figure 1. Transitions in the  ${}^1\Delta_{\rm g} + {}^3\varSigma_{\rm g}^-$  Band of Oxygen

## 5. CONTINUOUS ABSORPTION BY A'TMOSPHERIC GASES

Although not part of the data tape of primary concern in this report, a few words should be said about the relatively continuous regions of absorption of particular interest in the atmospheric "windows" near 2500 cm<sup>-1</sup> (4  $\mu$ m), from approximately 1250 cm<sup>-1</sup> to 700 cm<sup>-1</sup> (8  $\mu$ m - 14  $\mu$ m), and near 450 cm<sup>-1</sup> (22  $\mu$ m). In other spectral regions the contribution by nearby absorption lines is much greater than that by the continuum absorption, so that for practical purposes the continuum effect can be neglected, although it may be greater than in the windows.

This continuous absorption is caused by one or more of the following three processes: (1) extreme wings of strong collision-broadened absorption lines centered more than  $10\text{--}20~\text{cm}^{-1}$  away; (2) pressure induced absorption resulting from transitions that are forbidden for unperturbed molecules; and (3) the possible existence of the water dimer  $(H_20\text{:}H_20)$  in the case of the 8 to 14  $\mu\text{m}$  region.

The absorption coefficient due to continuum absorption can be expressed as

$$k = C_s P + C_b P_b \tag{22}$$

where  $\mathbf{C_s}$  is the self-broadened coefficient and  $\mathbf{C_b}$  is the foreign gas broadening coefficient, P is the total pressure and  $\mathbf{P_b}$  is the foreign gas pressure.

Figure 2 gives the spectral dependence of  $C_s$  for water vapor absorption in the 8 to 14  $\mu$ m region for three temperatures (Burch, 1970). The  $C_b$  value has been most reliably measured by McCoy et al, 1969, and is found for nitrogen to be  $C_b$ = 0.005 $C_s$  at room temperature.

Figure 3 gives the spectral dependence of  $C_s$  for the water vapor absorption in the region near 4  $\mu m$  for four different temperatures (Burch et al, 1971a). Note that the T=296  $^{\rm O}$ K curve is an extrapolation based on the measurements at higher temperature. These same workers found the ratio  $C_b/C_s$  for nitorgen broadening to be  $0.12\pm0.03$ .

Figure 4 gives the spectral dependence of the absorption coefficient due to the pressure-induced nitrogen absorption centered near 2330 cm<sup>-1</sup> (Burch et al, 1971a). Measurements have also been made by Shapiro and Gush, 1966, and Farmer and Houghton, 1966. Since the foreign gas broadening in this case results from a gas (oxygen) having a constant mixing ratio in the atmosphere, Eq. (22) reduces to

$$K = Const. \times P \tag{23}$$

Since the nitrogen abundance in the atmosphere is also directly proportional to P, the absorption depends on  $P^2$  and Figure 4 has as ordinate the absorption coefficient expressed in the units atm $^{-2}$  Km $^{-1}$ .

Since line wings as given by the Lorentz shape, Eq. (1), have been found to be in error in the extreme wings, an appropriate rule to follow for the truncation of

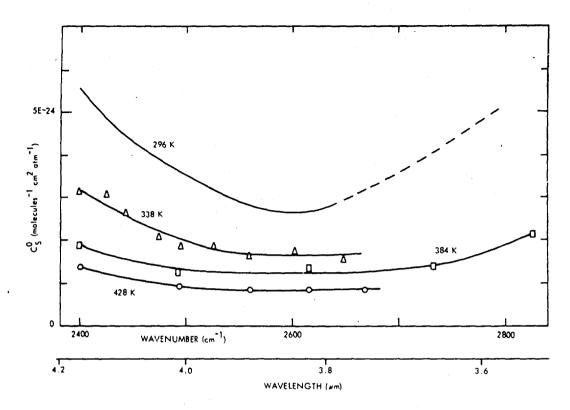


Figure 2. Normalized Continuum Absorption Coefficient for  ${\rm H_2O}$  at Three Temperatures

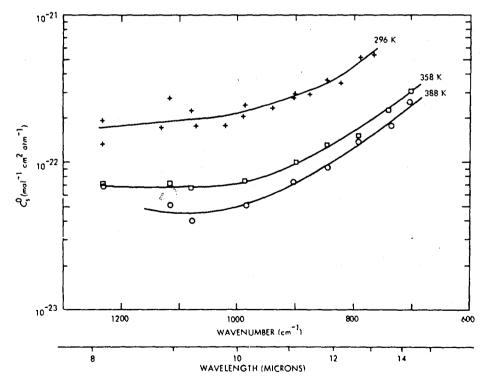


Figure 3. Normalized Continuum Absorption Coefficient Between 2400 and 2820 cm $^{-1}$  for Pure  $\rm H_2O$  at Four Temperatures

\$

line wings and the introduction of continuum absorption coefficients in accordance with Figures 2 through 4 is difficult to state. It is recommended that the user familiarize himself with this problem (see, for example, Burch et al, 1969) and in any case the use of the Lorentz shape beyond 20 or 30 wavenumbers of line centers is inappropriate (see also discussion on line shape on p. 3).

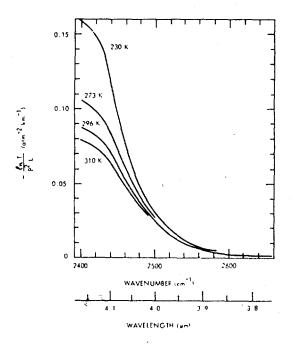


Figure 4. Spectral Plot of Absorption Coefficient for Atmospheric  $\rm N_2$  at Four Temperatures

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## Appendix A

Computer Program Listing for Reading Tape

```
PROGRAM RU TP( INPUT. OUTPUT, TAPES)
    DINENSION 2(400) + TT (15)
     4 = v
    150F=0
 24 전기루루드로 1V(2+U) (국(1)+국(3YU))
    IF (UVIT(2)) 25.30.35
 35 PRINT 35+TT(1)
 36 FORMAT(* PARITY ERROR AFTER *.F12.3)
    GO TO 2+
 30 IEOF=1-Jf+1
    PRINT 41.1EUF
 31 FORMAT (* EOF NO*+15)
     IF (IEDF . GT . 7) 30 TO 1001
     60 TO C+
 25 DECOUE (10.39.7(1)) IRED
 41 FORMAT(F10.3.E10.3.F5.3.F10.3.546.A5.13.14.13)
    1=1
 39 FORMAT(110)
    L=5
     00 40 K=1, IRED
     DECODE(80,41,8(L))(1T(I),1=1,13)
     PRINT 41. (TT(1).1=1.13)
    L=L+d
     IF(TT(1).LT.A) PRINT 153.A.TT(1)
      A=TT(1)
153 FORMAT(* OUT OF ORDER *+2F12.3)
 40 CONTINUE
     GO TO 24
1001 CALL EXIT
       STOP
      END
```

## Appendix B

Computer Program for Homogeneous Path Transmittance Calculation

The computer program (Program LBL) provided in this Appendix is intended for use as a check to ensure that a user of the AFCRL Data Tape will be using the data correctly. The spectral region chosen for a sample spectrum (Figure 5) contains spectral lines from four different atmospheric gases. The program was constructed for use with constant pressure and temperature paths only, so the user will be left to his own devices for real atmospheric applications. After computing transmittance at closely spaced monochromatic frequencies, a convolution is performed over a triangular slit function whose half-width can be chosen. Comment cards have been used freely, so no further discussion of this program will be given here.

: 1

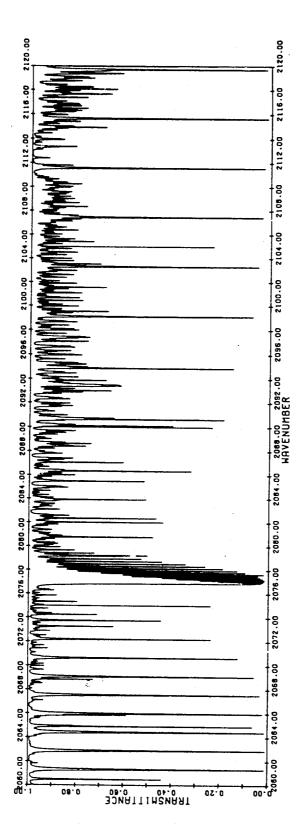


Figure B1

Synthetic Spectrum Generated using the Data Compilation. Conditions are as follows; pressure = 188 mb, T = 219K, W H<sub>2</sub>O = 2.00 x 10<sup>20</sup>, W<sub>CO<sub>2</sub></sub> = 2.05 x 10<sup>21</sup>, W<sub>O<sub>3</sub></sub> = 3.23 x 10<sup>18</sup>, W<sub>CO</sub> = 4.67 x 10<sup>17</sup>. Lines belonging to other molecular species contained on tape are not present in this spectral region. Spectral resolution is 0.01 cm<sup>-1</sup>.

```
DIMENSION W(7), R(325), GNU(3000), S(3000), A_PHA(3000), EDP(3000)
             DIMENSION MOL(3000), CAY1(7), 0^{5}D(3000), FNU(1000), TRANS(1000)
             DIMENSION SUMI(7) . CS2(7)
000000
             PROGRAM BY R. MCCLATCHEY.
             NO PUNCHED DECKS WILL BE DISTRIBUTED.
             THIS PROGRAM GENERATES A TRANSMITTANCE SPECTRUM WITH DUTPUT RESULITS
             PRINTED EVERY DELV WAVENUMBERS BETWEEN THE INITIAL FREQUENCY.
C
             VI. AND THE FINAL FREQUENCY. V2. CALCULATIONS ARE PERFORMED FOR
C
             A UNIFORM, CONSTANT PRESSURE, CONSTANT TEMPERATURE PATH CONTAINING
C
             ANY OR ALL OF THE MOLECULAR SPECIES DESCRIBED IN THIS REPORT
C
             IN ARBITRARY AMOUNTS. MOLECULAR ABUNDANCES MUST BE SPECIFIED
00000
             IN THE UNITS (MOLECULES/CM2). MONOCHROMATIC CALCULATIONS ARE
             MADE AT FREQUENCY INTERVALS. DV. A CRA TRIANGULAR SLIT FUNCTION
             OF HALF-WIDTH, A. IS CONVOLVED WITH THE MONOCHROMATIC RESULTS.
             IEOF=0
             DEPTH=0.001
             PI=3.14159
             SUM=0 + 0
             I V=1
             READ INPUT PARAMETERS (P=PRESSURE) . (T=TEMPERATURE) .
00000000
             W(1) = 420 + W(2) = C02 + d(3) = 03 + W(4) = 420 + W(5) = C0 + W(6) = C44 + W(7) = 02 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) = 420 + W(6) =
             VI AND V2 ARE FREQUENCY LIMITS FOR WHICH DUTPUT RESULTS ARE REQUIRED.
             DV IS MONOCHROMATIC FREQUENCY INCREMENT.
             BOUND IS THE FREQUENCY FROM ANY LINE CENTER BEYOND WHICH THE LINE
             WILL BE NEGLECTED.
             A IS THE HALF-WIDTH OF A TRIANGULAR SLIT FUNCTION.
             DELV IS FREQUENCY INCREMENT OF CONVOLVED OUTPUT TRANSMITTANCE
             RESULTS.
             READ 77. P.T
             PRINT 79. P.T
             READ 81, (W(M), M=1,7)
             PRINT 83
             PRINT 81+ (W(M)+M=1+7)
             VJ30+A+DUCB+VC+SV+IV +68 GA3R
             PRINT 87. V1.V2.DV.BOUND.A.DELV
             IF (A#2/JV+1.GT.3000) CALCULATION CANNOT BE DONE
             IF THERE ARE MORE THAN 3000 LINES READ FROM TAPE IN A FREQUENCY RANGE
             OF 2(A+JOUND) CALCULATION CANNOT BE DONE
             VBOT=V1-A-BOUND
             VTOP=V2+A+BOUND
             MFILE=9
             IF (VBnT.GE.500.0) MFILE=1
                                                                                                 NOT REPRODUCIBLE
             IF {VBO[.GE.1000.0) \| \text{WFILE=2}
             IF (VBO[.GE.2000.0) MFILE=3
                   (V801.GE.5000.0) MFILE=4
```

PROGRAM LBL (INPUT+OJTPUT+TAPEZ)

```
MFILE DÉTERMINES THE NUMBER OF ENDS OF FILE TO BE READ OVER
С
      BEFORE COMING TO THE PERTINENT DATA ON THE TAPE.
C
      . SAL CASE OF ACABA MCK BEA BM
С
      ILL=1
      BUFFER IN (2+0) (R(1)+R(325))
1
      IF (UNIT(2)) 7.5.3
      PRINT HJ. GNU(I)
3
      GO TO 1
      IEOF=IEOF+1
õ
      PRINT 91. IEOF
      IF (IEnf.GE.7) 60 TO 75
      GO TO 1
       IF (MFILE.GT.IEDF) 30 TO 1
7
      DECODE (10,93,8(1) ) IREC
      NT= (8 # T (EC) -6
       DECODE (10,95.R(NT) )TMAX
       IF (TMAX.LT.VBOT) GO TO 1
       L=5
       00 9 K=1+IREC
      DECODE (80.95.R(L) )GNU(I).S(I).ALPHA(I).EDP(I).IDAT.ISOT.MOLI(I)
       L=L+B
       IF (GNU(I).LT.V3OT) GO TO 9
       M=MOL([)
       PATH=5(1) #W(M)/(>I#0.06#P/1013.0)
       IF (PATH.LT.DEPTH) 30 TO 9
IF (GNU(I).GT.VTOP) GO TO 11
       I = I + i
 7
       CONTINUL
       IF (I.GT.2960) 30 TO 11
       GO TO 1
       I1=I
 11
       PRINT 97. VUOT. VTOP. GNU(I1).[]
       15=1
       VZP=GNU(II)-BOUND-A
 C
       TAPE HAS BEEN READ FOR ALL NECESSARY LINES OR FOR THE MAXIMUM NO.
 C
        OF LINES POSSIBLE SUBJECT TO RECYCLING.
 C
       HALFWIDTHS WILL BE SUPPLIED BELOW WHEN THEY DO NOT APPEAR
 С
        ON TAPE.
        DO 15 I=iLL.II
        M=MOL(I)
        IF (M.EQ.1) GO TO 15
          (ALPHA(I).GT.0.0) GO TO 13
        IF (M.EQ.2) ALPHA(I)=0.07
        IF (M.EQ.3) ALPHA(I)=0.11
        IF (4.50.4) ALPHA(1)=0.08
        IF (4.EQ.5) ALPHA(1)=0.06
        IF (M.E3.6) ALPHA(I)=0.055
        IF (M.EQ.7) ALPHA(I)=0.048
        IF (ALPHA(I).LT.0.01.0R.ALPHA(I).3T.1.0) ALPHA(I)=0.06
  13
```

```
15
      CONTINUE
      IS=1
      P0=1013.00
      10=246.00
      CS1 = (T0 - T) / (T0 + T + 0.5946)
C
      ROTATIONAL PARTITION FUNCTION IS DEFINED BELOW
С
      DO 21 4=1.7
      IF
         (M.EQ.1) GO TO 17
         (4.E4.2) GD TD 19
      ΙF
      IF (4.60.3) GO TO 17
      IF (M.EQ.4) GO TO 19
      IF (M.EQ.5) GO TO 17
      IF (M.EJ.6) GO TO 17
      IF (M.EQ.7) GO TO 19
17
      CS2(M) = ((T0/T) **1.5)
      GO TO 21
19
      CS2(4) = F0/T
21
      CONTINUÉ
      CA={(T0/T) ##0.5) #(P/P0)
C
      TEMPERATURE DEPENDENCE OF ALL LINE INTENSITIES COMPUTED HERE.
C
      DO 23 [=ILL+II
      M=MOL(I)
      S(I)=S(I)*CS2(M)*EXP(-EDP(I)*CS1)
23
      ALPHA(I)=ALPHA(I) *C4
      V=V1-A
25
      Do 27 4=1.7
      CAY1(M)=0.0
27
      SUM1 (M) =0.0
С
      DETERMINE INDICES (15 AND 16) INDICATING WHICH SPECTRAL LINES
C
      ARE TO SE USED IN THE CALCULATION AT FREQUENCY V.
С
      DO 33 I=I5+11
      IF (V-RJUND-GNU(I)) 29,29,33
29
      I5=I
      GO TO 35
33
      CONTINUE
      I5=I1
      GO TO 47
      DO 39 J=15+11
35
      IF (V+90UND-GNU(J)) 37+37+39
      16=J-1
37
      GO TO 43
37
      CONTINUE
      I6≃II
С
      COMPUTE THE OPTICAL DEPTH AND TRANSMITTANCE AT FREQUENCY V.
C
43
      DO 45 1=15.16
      M=MOL(I)
```

```
Z=ABSEV-GNU(I))
                     SUMI(M) = S(I) + ALPHA(I) / (Z**2+ALPHA(I) **2)
                    CAYI (M) = CAYI (M) + SUMI (M)
 45
                    CONTINUE
                    CAY=0.0
                    DO 47 M=1.7
                    CAY=CAY+CAY1(M) *W(M)
 47
                    OPD(IV) = CAY+0.3183
                    50 TO 51
49
                    0.0=(VI) G90
51
                    (VI)CQC-)QX=(VI)QQO
                    IF ((V+JV).GT.V2=) 30 TO 53
                    IF (V.SE.V2+A) 30 TO 53
                    IF (IV.GE.3000) 30 TO 53
                    I \lor = I \lor + 1
                    VC+V=V
                    GO TO 25
                    THIS POINT. CYCLE BACK TO STATEMENT 35 AND COMPUTE THE STATE POINT. STANCHDONOM OF THE STATE POINT STANCE OF THE STATE POINT TABLE OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF THE STATE POINT OF
C
                    IF STATEMENT 53 IS REACHED FALL POSSIBLE MONOCHROMATIC TRANSMITTANCE VALUES HAVE BEEN COMPUTED. AND THE SLIT FUNCTION CONVOLUTION WILL!
000
                    NOW DE PERFORMED IN LOOP 57
53
                   FREQ=VI
                    PRINT 101+ IV+V+V2P
                    FINAL=V1+3000.*DV-A-DELV
                    V=V1-A
                    JFNU=1
                    L=DELV/JV+0.01
                    IA=1
                    SUM=0.0
วิวั
                    VI+AI=I 16 CC
                    SUM=SUM+ (A-ABS (V-FREQ)) #OPD (T)
                    VC+V=V
                    IF (V-(FREQ+A)) 57,59,59
57
                    CONTINUE
                    TRANS(JFNU)=SUM+)V/(A+A)
59
                   FNU (JFNJ) =FREQ
                    IF (FREG.GT.V2) 30 TO 61
                    IF (FREJ.GT.V2P) GO TO 51
                    IF (FREU.GE.FINAL) GO TO 61
                    FREQ=FP=Q+DELV
                    IF (JFNU.GE.1000) GO TO 61
                    JFNU=JFNU+1
                    IA=IA+L
                   V=FREQ-A
                   SUM=0.0
                   GO TO 5>
Ċ
                   CONVOLVEU TRANSMITTANCE RESULTS ARE NOW PRINTED OUT.
С
                    PRINT 103, JFNU
5 i
                    PRINT 104
```

```
PRINT 105+ (FNU(J)+TRANS(J)+J=1+JFNU)
      IF (FREQ.GE.V2) 30 TO 75
      IF (FREG.GT.V2P) GO TO 67
      IF (JFNU.GE.1000) GO TO 65
      IF (FREQ.GE.FINAL) 30 TO 63
      GO TO 75
53
      V1=FINAL+DELV
      15=1
      I \vee = 1
      JFNU=1
      V=V1-A
      GO TO 25
55
      IA=IA+L
С
      IF STATEMENT 65 IS REACHED. ADDITIONAL MONOCHROMATIC CALCULATIONS
C
C
      ARE REQUIRED TO SATISFY THE TOTAL FREQUENCY RANGE OVER WHICH
C
      CONVOLVED RESULTS ARE REQUIRED.
C
      JFNU=1
      V=FREQ-A
      GO TO 53
57
      Iv=1
С
      IF STATEMENT 67 IS REACHED. THE DATA FROM THE DATA TAPE WILL BE
CC
      REORGANIZED AND THE TAPE WILL BE READ AGAIN.
      JFNU=1
      V1=FREO
      DRUDB-A-1V=TCEV
      DO 69 14=1+11
      IF (GNU(IN).GT.V30T) GO TO 7]
      CONTINUE
64
      IN=II
71
      VI=LI
      L=1
      DO 73 [=1J+I1
      GNU(L)=3NU(I)
      S(L)=S(1)
      ALPHA(L) = ALPHA(I)
      EDP(L) = EDP(I)
      1) JCP=(1) JOM
73
      L=L+1
      I=L
      ILL=L
      GO TO I
7 o
      CALL EXIT
      STOP
77
      FORMAT (£12.5.F7.2)
      FORMAT (* PRESSURE = * . E12.5 . * TEMPERATURE = * . F7.2)
79
      FORMAT (7E10.3)
51
      FORMAT (3X+#WATER++6X+#COZ++6X+#OZONE#+7X+#N2O#+7X+#CO#+8X+#CH4#+7
83
      1X+#02#+4X)
      FORMAT (6F10.3)
35
```

```
37
       FORMAT (* V1 =*,F10.3,*V2 =*,F10.3,*DV=*,F10.3,*BOUND =*,F10.3,*A
      I=+,F10.3.*DELV =+.F10.3)

FORMAT (* PARITY ERROR ENCOUNTERED AT*,F12.3)

FORMAT (* END OF FILE ENCOUNTERED*,I5)
89
91
93
       FORMAT (I10)
95
       FORMAT (F10.3.E10.3.F5.3.F10.3.35X.13.14.13)
       FORMAT (# VBOT = ** F12.3 ** VTO = ** F12.3 ** GNU = ** F12.3 ** I1 ** IB)
97
101
       FORMAT (15+2F10.4)
103
       FORMAT (# JFNU =#+I5)
104
       FORMAT (5(# FREQUENCY
                                    TRANS.
                                                #))
105
       FORMAT (5(F10.3,E12.5))
       END
```

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